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VOLUME XXXVII 1920

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE THIRTY-SEVENTH GENERAL MEETING OF THE SOCIETY, HELD IN BOSTON AND CAMBRIDGE, MASS., APRIL 8, 9 AND 10, 1920.

There were 149 members registered and 124 guests, a total of 273 participants.

PROCEEDINGS OF WEDNESDAY, APRIL 7, 1920

Registration started at 6.00 P. M. in the lobby of the Copley Plaza Hotel, for the convenience of early arriving members and guests.

At 8.30 P. M. the Directors of the Society assembled in Rogers Building of the Massachusetts Institute of Technology to hold the regular Board Meeting.

PROCEEDINGS OF THURSDAY, APRIL 8

At 9.30 A. M., President Bancroft called the meeting to order in Huntington Hall, Rogers Building, one of the old "Technology" buildings, and presented Professor Talbot, who welcomed the visitors on behalf of the Institute. After thanking Prof. Talbot for his kind words of welcome, the annual business meeting of the Society was opened. Secretary Richards read the report of the Board of Directors, including the reports of the Secretary and the Treasurer. These reports will be found appended to the Proceedings.

The question of the Society's approving the establishment of the Metric System as the only legal standard of weights and

measures in the United States was brought up and by motion referred to a referendum of the Society, as a guide to the Board of Directors in taking action for the Society.

President Bancroft announced the death in February, 1920, of Professor Henry S. Carhart, the second president of the Society, and presented the following resolution:

Resolution Concerning the Death of Henry S. Carhart.

WHEREAS, The Board of Directors of the American Electrochemical Society learns with deep regret of the death of Dr. Henry S. Carhart, at Pasadena, California, on February 13, 1920; and

WHEREAS, Dr. Carhart, Professor Emeritus of Physics, University of Michigan, took an active part in the welfare of this Society during its early days when its future success depended so greatly on its support by those who, like Dr. Carhart, had a national reputation for creditable work done in the science of electrochemistry; and

WHEREAS, Dr. Carhart was its second president, in 1904-5, and contributed to it several papers during the early years of the Society; therefore be it

Resolved, That the Board of Directors expresses its deep regret at the loss of one of its oldest, most prominent and valued members, and hereby extends its sincere sympathies to his family.

(Signed) W. D. BANCROFT, *President,*
(Signed) J. W. RICHARDS, *Secretary.*

The Chair then called for the report of the Tellers of Election, which in the absence of the Tellers was opened by Secretary Richards and presented as follows:

REPORT OF TELLERS OF ELECTION

Following is a list of votes cast in the election of officers for the year 1920-1921:

President: W. S. Landis, 264; Acheson Smith, 82.

Vice-Presidents: J. A. Mathews, 271; L. E. Saunders, 258; A. T. Hinckley, 237; F. C. Frary, 95; F. A. J. FitzGerald, 69; A. H. Hooker, 57; W. S. Landis, 40; A. D. Little, 1.

Managers: Colin G. Fink, 282; Acheson Smith, 232; H. B. Coho, 171; L. H. Baekeland, 134; H. W. Gillett, 89; Robt. Turnbull, 88; C. F. Hirshfeld, 22.

Treasurer: Pedro G. Salom, 340.

Secretary: Jos. W. Richards, 337; H. B. Coho, 1; F. A. Lidbury, 1; F. A. J. FitzGerald, 1.

Signed:

BARRY MACNUTT,
ALLISON BUTTS,
S. S. SEYFERT.

The President announced the following elections, as the result of the report of the Tellers:

President: Walter S. Landis.

Vice Presidents: J. A. Mathews, L. E. Saunders, A. T. Hinckley.

Managers: Colin G. Fink, Acheson Smith, H. B. Coho.

Treasurer: Pedro G. Salom.

Secretary: Jos. W. Richards.

The scientific business of the meeting began with an address by the retiring president, Prof. Bancroft, on "Contact Catalysis." This was followed by a "Symposium on Colloid Chemistry" in charge of Prof. Bancroft. The contributions to this symposium were by W. D. Bancroft, W. A. Deane, G. A. Hulett and O. H. Nelson, W. A. Selvig and W. C. Ratliff, and by Wm. C. Moore. The other papers presented at this session were by H. M. Goodwin and Max Knobel, H. D. Holler and L. M. Ritchie, D. A. MacInnes, L. Adler and D. B. Joubert, and by Wm. Roy Mott. All these papers are printed in full in these Transactions, together with their discussions.

After lunch, taken in the Walker Memorial Building, the afternoon session was held in one of the lecture rooms of the new Institute of Technology buildings in Cambridge. Papers were presented by the following and discussed as printed in these Transactions: W. S. Landis, C. J. Rottmann, T. D. Yensen, L. T. Richardson, S. C. Langdon and M. A. Grossman, P. H. Brace, Geo. J. Sargent, F. C. Mathers and Stanley Sowder, M. L. Hart-

mann and O. A. Hougen, M. L. Hartmann and J. F. Kobler. After this session the visitors were guided through the magnificent new buildings of the Institute.

In the evening, Arthur D. Little, Inc., was host to the Society at its model industrial research laboratories in Cambridge. The museums, library, laboratories and semi-commercial plant in the basement were admired by a gathering which literally filled the building. Later, there were speeches and singing and a good deal of fun, with unlimited smokes, and Professor Armstrong, of the Massachusetts Institute, entertained most charmingly with a pictorial account of hunting with a camera in the wilds of New Brunswick. He delighted and enthused his audience by his breezy account of a most fascinating summer vacation.

PROCEEDINGS OF FRIDAY, APRIL 9

Friday was set for joint sessions with the American Institute of Electrical Engineers. The program was a morning session with a Symposium on Electrically Produced Alloys, an afternoon trip to the General Electric Works at Lynn, an informal subscription dinner, followed by an evening session with a Symposium on Power for Electrochemical Purposes. President Bancroft was chairman at the morning session and President Townley, of the Electrical Engineers, in the evening.

At the morning session, in the Symposium on Electrically Produced Alloys, papers by the following were read and discussed: H. E. Howe, R. J. Anderson, C. B. Gibson, B. D. Saklatwalla, Elwood Haynes, F. A. Raven, R. M. Major, R. C. McKenna, Alcan Hirsch, M. A. Hunter and J. W. Bacon, C. F. Harding, and by T. D. Yensen. With the exception of the last two (published by the A. I. E. E.) all these papers with discussions are printed in full in these Transactions.

The trip to Lynn was made in eight electric cars, directly from and returning to Copley Square, both societies being invited guests of the General Electric Company. A printed itinerary gave all the details of the visit with great accuracy, and it was carried out according to plan with military precision.

The informal dinner was attended by about a hundred and fifty, and was graced by the presence of our esteemed friend, Professor Elihu Thompson.

In the Symposium on Power for Electrochemical Purposes, at the evening session, papers by the following were presented and discussed: E. A. Wilcox, H. L. Hess, A. C. Smith, W. G. Berlin, C. T. Maynard, F. H. Fowler, J. W. Beckman. These papers with ensuing discussions are printed in full in these Transactions. The American Institute of Electrical Engineers was represented with papers by J. L. Harper, H. A. Winne and J. A. Seede.

PROCEEDINGS OF SATURDAY, APRIL 10

The meeting was called to order in the New Lecture Hall at Harvard University, Cambridge, at 9.30 A. M., by President Bancroft. Dr. T. W. Richards welcomed the Society with the following words:

T. W. RICHARDS: "It is a great pleasure to welcome you fellow-members of the American Electrochemical Society and your distinguished President at Harvard once more. The intervening years, since the last time you came hither, have been filled with many events and with great progress in electrochemistry. They have not diminished, indeed, they have very greatly increased our appreciation of the very great importance of electrochemistry to the future of industry and of civilization. There is an interesting historical reason why the American Electrochemical Society should come here occasionally. Our University cannot lay claim to having been the cradle of electrochemistry, but she can lay claim to having been one of the chief inspiring influences in the life of the man who built the cradle. About a hundred and fifty years ago Benjamin Thompson walked from North Woburn to Harvard Hall (ten or more miles) to hear John Winthrop's lectures on natural philosophy. Unquestionably those lectures, of which Count Rumford's notes are still in the physical laboratories here, formed a great part of the stimulus which afterwards led him to take so much interest in physical science and in the usefulness of science in general. About 30 years afterwards he founded The Royal Institution, which was, of course, really the cradle of electrochemistry, and without which the work of Davy and Faraday could hardly have been carried out.

"I do not need to point out to you the fact that Davy and Faraday worked without any idea of practical application, but you know better than anybody else how important are the applications

of those principles which they discovered. There is not any need for me to draw the moral as regards the connection between pure science and applied science; you know it very well. Indeed, I have come here not to talk to you but rather to listen. Once more I want to greet you very cordially, to welcome you to Harvard, and to wish the American Electrochemical Society long life and happiness."

President Bancroft responded appropriately to the warm words of welcome spoken by Dr. T. W. Richards, and then proceeded to the technical part of the session. Papers by the following were read and discussed and are printed in these Transactions: J. W. Richards, C. A. Keller, P. B. Short, H. M. St. John, L. B. Lindemuth and E. F. Kern.

After the technical part of the session Secretary Richards presented a resolution in regard to the publication in this country of Critical Tables of Physical Constants.

J. W. RICHARDS: I think that we are all interested, at least we were all interested during the war, in the fact that we could not get reliable tables of physical and chemical constants, our usual supply of those being shut off, and we are at present all interested in the fact that the National Research Council has undertaken to supply this want in the future with critical tables of chemical and physical data. I therefore bring forward this resolution for consideration by the Society:

Resolution on Publication of Critical Compendia of Physical Constants.

WHEREAS, Every industry for its successful operation depends upon an accurate knowledge of the properties of the materials it uses and produces, and numerical values of these properties which are known as their Constants; and,

WHEREAS, During the war, it became evident that much of the published data on these Constants were found to be extremely inaccurate, entailing considerable loss in time and money, and it was found in many cases that data very much desired were not to be found in published records; and,

WHEREAS, Up to now, publications of such Constants in tabular form have been mostly in a foreign language, and consequently, of limited availability; and,

WHEREAS, Under allotment by the Inter-Allied Council, the National Research Council of the United States, (an organization duly created by act of Congress) has decided that this deficiency could best be met by the compilation and publication in English of Tables of Constants, which have been critically revised as to their accuracy, and have decided that this could best be done by the appointment of a committee to act as trustees in charge of such compilation, and as far as is necessary to have charge of the determination of such Constants as have not already been published or determined; and,

WHEREAS, The Trustees so appointed were selected as representing the American Chemical Society, the American Physical Society and the American Institute of Chemical Engineers, the representatives being respectively Julius Stieglitz, Edwin P. Hyde and Hugh K. Moore; therefore be it

Resolved, That the American Electrochemical Society in convention assembled heartily endorses the project and assures the Trustees of its support in every way within its power.

April 10, 1920.

T. W. RICHARDS: I quite agree that tables, critical or otherwise, are of the utmost importance, but a great deal depends upon the quality of the criticising. There is a risk that unless those tables are put into very expert hands, important results may be cast aside for lack of intimate knowledge of the specific problems in question. Therefore I think that the National Research Council ought to be strongly urged to give references to *all* the data concerning any given subject. Supposing that some of them are discredited; at least we ought to have a chance to find why they are discredited and to know where to find them. I am earnestly in favor of having the Council publish the tables, but their value must depend on their nature.

W. D. BANCROFT: The ears of the National Research Council happen to be here—I am it. (Laughter.) It is not proposed to give simply one value for any particular constant; it is proposed, as I understand it, to give all the values which are presumably worth while. I do not understand that Mr. T. W. Richards would necessarily include every single determination of everything, because that would be distinctly

superfluous; on the other hand, those of us who have used Landolt and Börnstein's Tables have been very much puzzled to know which value was probably the better when we did not have any particular knowledge of the subject ourselves, and consequently it is proposed to put each table or each separate determination in the hands of the best experts or the best group of experts that can be found among the nations supporting the tables, and to have that expert or group of experts pick out the particular figure, which, in his opinion, is the most probable value at that date. I assume that the authority will be given for it; that is, that Millikan, of Chicago, will determine one thing, etc., etc. That seems to me to meet the difficulties. As you know, the thing has been done for years in regard to the atomic weight determinations, a subject of which Mr. Richards has heard; and while it is very likely that everybody does not agree with the values selected by the committee each particular year, yet it is a distinct advantage, I think, to have values which are apparently considered the best. It seems to me that it has the other advantage that, if you do not agree with them, you are in a position to get up and say that you think the decision of the committee is wrong and to give reasons for it; whereas, if you have got to shoot at a dozen different values, you will not get anywhere. It does not seem to me that this in any way binds anybody to accept any values as being necessarily right; it is merely that we are hoping to do for all the data what has already been done, fairly successfully, I think, in regard to the atomic weight determinations; and certainly my own experience in using Landolt and Börnstein's tables when I wanted to get at some figure or other, was that I should have welcomed a statement as to which was the most probable value, as being of great help. It seems to me that the whole thing is being taken care of pretty fairly satisfactorily. That is not, of course, saying that no mistakes have been made, but it does seem to me that the plan as proposed is a better plan than the one adopted in Landolt and Börnstein's tables and in subsequent editions thereof.

T. W. RICHARDS: I quite agree with the President that it is exceedingly helpful to have the advice of an expert on such things. I did not in the least mean that a single figure should not be singled out as the most probable; all I am asking is that the other

figures be given with references, so that those who believe themselves to be experts not so very far different from the experts who make the decision, may have a chance to decide for themselves. I do not mean to say that I am in that class myself; but I can easily conceive that such a case may arise. I have heard more than one person make this suggestion in private.

W. D. BANCROFT: I agree entirely with Mr. Richards' point of view, and I should like to add that I think it is a very self-sacrificing attitude on his part, because it means that he is going to put himself up as the target for people to come along and see if they cannot change his data, which the committee has adopted as official.

W. R. MOTT: I think that all data should be designated as to three classes of reliability; *A* for the best, *B* for the second best, and *C* for the poorest class. The volume of data on a particular constant may be very large or very small. A very bad case of not weighing the volume and nature of evidence on a particular constant is the current quotation in Landolt, and all other tables of constants, of the melting point of strontium fluoride as 902° C. (Carnelley, 1878) while the identical figure for the melting point of calcium fluoride has long been abandoned. The figures in both cases are wrong by hundreds of degrees and should be designated as very poor.

SECRETARY RICHARDS: I would like to ask if the chairman can inform us whether these tables will be gotten out in co-operation with the annual tables of constants which appear every year from Paris and which give us yearly the new data. If this new volume were issued every five years, let us say, it would serve most usefully to collect in one volume periodically the required data, the other volumes giving us each year the additional values.

W. D. BANCROFT: One essential difference between the two is that the annual tables, which will continue to be issued by the French, are not critical, and these other data will at least have an official label on them; they may not be right, but they will be labelled officially. As a matter of fact, there is no need of worry as to any probable conflict between these two sets of tables, because the motion to assign the work of getting the critical tables to the United States was made by Mr. Marie, who is in charge of the other tables.

After this discussion the President called for a vote on the resolution, which resulted in its unanimous adoption.

Dr. Carl Hering then offered the following resolution of thanks, which was heartily endorsed and unanimously adopted.

Resolution of Thanks.

The American Electrochemical Society, closing its Thirty-seventh General Meeting, in Boston, wishes to place on record its appreciation of the co-operation received from local agencies and firms, which contributed materially to the success of the meeting, in particular as follows:

The General Electric Company, for the very well organized and satisfactory visit to its works at Lynn, and the courtesy and usefulness of its staff acting as guides.

The Huff Electrostatic Separator Company, for opening its plant to visit by the Society.

The Arthur D. Little, Incorporated, for a highly enjoyable and instructive evening spent in its model laboratories.

The Governing Board of the Massachusetts Institute of Technology and the Corporation of Harvard University, for the hospitality extended in the use of their halls, lecture rooms and dining halls.

The Copley Plaza Hotel, for furnishing facilities for registration.

The Ladies' Committee, for the very efficient and enjoyable hospitality and entertainment extended to visiting ladies.

The Local Committee in charge of the meeting, for its time and energy expended upon the various details of the meeting.

The Electro-Metallurgical Co. of America, Mr. F. A. Raven, the Vanadium Corp. of America, the United Lead Co., the Anaconda Copper Co., the Haynes Stellite Co., and Mr. G. B. Hogaboom, for exhibitions of metallurgical and electrochemical specimens to illustrate the proceedings of the meeting.

Secretary Richards made then a few announcements about the program for the afternoon, whereupon President Bancroft declared the Thirty-seventh Meeting adjourned.

After the session, Professor T. W. Richards invited those present to inspect the Gibbs Research Laboratory, which opportunity was eagerly accepted. Lunch followed at the Harvard Union.

A most interesting visit to the Huff Electrostatic Separator plant at Arlington closed the program.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

The following are some of the important items of business transacted by your Board of Directors during the past year:

It was ruled that the Publications of the Society adopt *pro tem* the negative sign as the sign of the potential of the zinc electrode until such time that the matter shall be more definitely settled. This involves that electric potential signs will be changed in papers accepted for publication, if they do not conform with this ruling of the Board. In such cases a note will be affixed to the paper to the effect that the negative sign has been arbitrarily given to the potential of the zinc electrode in order that uniformity might prevail in this respect in the papers published in our Transactions.

The monthly secretarial appropriation was on motion increased to $300.

An appropriation of $100 was made to meet the expenses of the Booth of our Society at the Chemical Exposition at Chicago.

A resolution was passed protesting against the abolishment of the Chemical Warfare Service, and it was ordered that copies of the resolution be sent to the military authorities and to the members of Congress.

The usual annual contribution of $50 was voted to the Annual Tables of Physical and Chemical Constants for 1919.

At the instance of the Librarian of Congress, a complete set of our Transactions bound in cloth was donated to the University of Louvain for the restoration of their Library.

The sum of 187.50 francs was appropriated as dues to the International Chemical Union, to be paid through the National Research Council of Washington, D. C.

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1919 the Society held two general meetings, one in New York City, April 3d to 5th, at which the attendance

was 213 members and 123 guests, total 336; the second at Chicago, September 23d to 26th, at which were registered 242 members and 136 guests, total 378. At the Spring Meeting in New York City 24 papers were presented and at the Fall Meeting in Chicago 18 papers.

During the year Volumes XXXIV and XXXV have been printed and distributed.

The edition of Volume XXXIV was 2,100 copies, as follows: 1,550 copies complete, bound in cloth, 250 copies bound in paper for distribution to the Faraday Society, 250 copies unbound to be kept in stock, and 50 extra copies for distribution in pamphlet form to authors of papers.

The edition of Volume XXXV was 2,200 copies, as follows: 1,650 copies complete, bound in cloth, 250 copies bound in paper for distribution to the Faraday Society, 250 copies unbound to be kept in stock, and 50 extra copies for distribution in pamphlet form to authors of papers.

The stock of Volumes on hand December 31, 1919, was as follows:

Volume	Bound in Cloth	Bound in Paper	Total
I	158	13	171
II	158	0	158
III	78	0	78
IV	86	233	319
V	36	234	270
VI	126	10	136
VII	49	195	244
VIII	41	321	362
IX	93	315	408
X	97	244	341
XI	89	266	355
XII	72	254	326
XIII	137	15	152
XIV	169	17	186
XV	172	223	395
XVI	175	288	463
XVII	98	519	617
XVIII	104	522	626
XIX	158	331	489

Volume	Bound in Cloth	Bound in Paper	Total
XX	168	334	502
XXI	162	353	515
XXII	162	305	467
XXIII	165	293	458
XXIV	313	0	313
XXV	424	37	461
XXVI	165	377	542
XXVII	5	537	542
XXVIII	158	374	532
XXIX	115	554	669
XXX	225	28	253
XXXI	106	31	137
XXXII	94	283	377
XXXIII	96	250	346
XXXIV	178	257	435
Index	262	68	330

Financial Statement.

Receipts in 1919.

Cash Assets beginning 1919 account		$4,337 10
Entrance Fees	$1,925 00	
Current Dues	8,700 00	
Volumes 1919	5,200 10	
Back Dues 1918	620 00	
Volumes 1918	320 00	
Advance Dues 1920	1,505 00	
Volumes 1920	860 00	
Advance Dues 1921-23	15 00	
Sale of Publications	2,114 23	
Sale of Reprints	573 66	
Sale of Membership Certificates	33 22	
Sale of Society Pins	199 75	
Return of Contribution to War Committee of Tech. Societies	247 50	
Payment for 1917 volumes by Faraday Society	506 15	
Subscription to Faraday Society's Transactions	213 75	
Interest on local Bank Account	75 59	
Interest on Philadelphia Bank account	69 38	
Interest on Philadelphia Electric Bonds	155 00	
Interest on Liberty Loan Bonds	382 18	
		23,715 51
		$28,052 61

EXPENDITURES IN 1919.

Secretarial Appropriation	$3,000 00	
Office Printing	686 78	
Printing of Volume 33	2,392 45	
Printing of Volume 34	2,947 23	
Printing of Advance Copies and Discussions	4,205 76	
Engraving	671 21	
Extra Reprints	686 27	
Compiling and Printing of Electrochemical Reference List	453 33	
Binding of Back Volumes	129 50	
Office Postage	353 54	
Postage on Advance Copies and Bulletins	678 16	
Express and Postage on Volumes	273 12	
Office Expenses	1,184 88	
Expenses of Meetings	841 38	
Office Equipment	243 00	
Storage and Insurance	222 12	
Membership Committee	1,757 57	
Publication Committee	14 43	
Booth Committee	100 00	
Local Sections	500 00	
Rebate to Faraday Society on 1917 volumes	263 50	
Contribution to "Annual Tables of Phys. and Chem. Constants"	50 00	
Gold Society Pins	266 99	
Miscellaneous	10 00	
Investment in Liberty Bonds	2,000 00	
		$23,931 22
Cash assets beginning January, 1920, account		4,121 39
		$28,052 61

Condition of Membership of the Society in 1919.

Members January 1, 1919		1,903
Elected and qualified as members in 1919		401
		2,304
Resignations in 1919	28	
Deaths in 1919	7	
Dropped for non-payment of dues in 1919	60	
		95
Members December 31, 1919		2,209
Net increase for calendar year		306

Condition, April 7, 1920.

Members January 1, 1920		2,209
Qualified as members to April 7, 1920		197
		2,406
Deaths	6	
Dropped for non-payment of dues	93	
		99
Members April 7, 1920		2,307
Members April 2, 1919		1,928
Net increase		379

TREASURER'S ANNUAL REPORT, 1919

January 1, 1919, cash balance	$4,337 10	
Total receipts for 1919	23,715 51	
		$28,052 61
Total expenditures, 1919		23,931 22
Balance, December 31, 1919		$4,121 39

We have examined the above statement of account, receipts and expenditures for the year 1919, and find the same to be correct.

We also report the following securities of the Society in the Safe Deposit Vault of the Commonwealth Title Insurance & Trust Co., Philadelphia, Pa.:

Philadelphia Electric Co. 5's	$3,100 00
1st Liberty Loan	2,000 00
2nd Liberty Loan	2,000 00
3rd Liberty Loan	2,000 00
4th Liberty Loan	2,000 00
5th Victory Loan	2,000 00
	$13,100 00

(Signed) CARL HERING,
(Signed) S. S. SADTLER,
Auditors.

MEMBERS AND GUESTS REGISTERED AT THE THIRTY-SEVENTH GENERAL MEETING

Members.

W. G. Allan
Arthur N. Anderson
F. Clarke Atwood
R. O. Bailey
R. E. Baker
W. D. Bancroft
F. E. Bash
C. E. W. Bateson
F. B. Bayless
E. A. Beck
F. M. Becket
E. O. Benjamin
G. M. Berry
Wm. Blum
J. C. Bradley
F. W. Brooke
W. K. Brown
A. R. Bullock
F. F. Burr
D. C. Burroughs
G. Campbell
J. Campbell
S. C. Carrier
D. F. Calhane
N. K. Chaney
H. C. Chapin
J. L. Christie
G. H. Clevenger
E. A. Colby
E. F. Cone
Herman C. Copper
V. G. Converse
J. H. Critchett
E. L. Crosby
A. S. Cushman
R. E. Dennis
P. K. Devers
C. G. Fink
F. A. J. FitzGerald
Frederick Flagg
J. A. Fogarty
F. C. Frary
J. A. Gann
W. H. Gessell
A. E. Gibbs
C. B. Gibson
H. W. Gillett
G. C. Given
J. B. Glaze
H. M. Goodwin
J. S. Gravely
M. L. Griffin
C. Hambuechen
J. L. Harper
W. E. Harrison
Carl Hering
Henry Hess
A. T. Hinckley
A. Hirsch
A. K. Hobby
F. Hodson
Geo. B. Hogaboom
R. P. Hommel
A. T. Hyde
L. E. Imlay
G. Jones
L. C. Judson
F. R. Kemmer
Th. E. Kendrick
Ivor Kenway
D. B. Keyes
R. H. Kienle
J. A. King
M. Knobel
W. Laib
H. A. Lavene
A. D. Little
R. A. Long
R. E. Lowe
D. A. Lyon
D. A. MacInnes
W. E. McKee
J. McKinley
W. A. McKnight
H. L. McQuaid
P. A. McTerney
C. P. Madsen
C. G. Maier
A. B. Miller
D. D. Miller
D. R. Miller
L. B. Miller
H. S. Miner
W. C. Moore
W. E. Moore
H. E. Morse
Wm. Roy Mott
James Munn
A. Nagelvoort
E. F. Northrup
J. D. Noyes
E. G. Nutting
A. B. Oatman
H. C. Parmelee
E. B. Peck
O. A. Pickett
E. C. Pitman
L. N. Reed
A. G. Reeve
H. G. Reist
Albert E. Rhoads
J. W. Richards
T. W. Richards
C. N. Richardson
F. D. S. Robertson
E. S. Ross
C. F. Roth
C. G. Ruffner
B. D. Saklatwalla
L. E. Saunders
W. M. Saunders
P. G. Savage
C. G. Schluederberg
W. S. Scott
J. E. Seede
H. J. Skinner
A. Smith
F. A. Stamps
D. C. Stockbarger
H. Styri
S. Temple
M. deKay Thompson
N. J. Thompson
A. E. Thurber
J. H. Thurber
L. S. Thurston
S. A. Tucker
M. Unger
W. H. Walker
F. S. Weiser
Jens Westly
D. Willcox
C. E. Williams
A. M. Williamson
C. A. Winder
H. A. Winne
W. W. Winship
W. J. Wooldridge
R. E. Zimmerman

Guests.

R. J. Anderson, Pittsburgh, Pa.
H. V. Atwell, Niagara Falls, N. Y.
J. A. Aupperle, Middleton, Ohio
C. W. Babcock, Boston, Mass.
R. L. Baldwin, Niagara Falls, N. Y.
Th. Bartram, Boston, Mass.
G. P. Baxter, Cambridge, Mass.
O. Benzanson, Woburn, Mass.
R. N. Blakeslee, Jr., Bridgeport, Conn.
F. J. Blaney, Newark, N. J.
C. A. Blatchley, New York City
J. J. Bloomfield, Durham, N. H.
C. H. Booth, Chicago, Ill.
P. H. Brace, Pittsburgh, Pa.
R. L. Bracewell, Springfield, Mass.
A. E. Bradley, Boston, Mass.
H. L. Bradley, Boston, Mass.
A. F. Braid, New York City.
Isabelle Briggs, Flushing, N. Y.
T. L. Briggs, New York City
D. J. Burke, Syracuse, N. Y.
A. R. Cade, Fremont, Ohio
Mrs. A. R. Cade, Fremont, Ohio
O. D. Cany, Long Island City
E. H. Chaney, Cambridge, Mass.
W. Y. Chin, Shanghai, China
E. R. Coe, Bridgeport, Conn.
Mrs. E. A. Colby, Newark, N. J.
J. B. Conant, Cambridge, Mass.
E. L. Crans, Boston, Mass.
Mrs. E. L. Crosby, Detroit, Mich.
W. A. Deane, New York City
H. A. de Fries, New York City
B. H. De Long, Reading, Pa.
A. W. Derumber, Pittsburgh,, Pa.
R. W. Dodge, Portland, Me.
Walter C. Durfee, Boston, Mass.
Winthrop C. Durfee, Boston, Mass.
J. D. Edwards, Pittsburgh, Pa.
Mrs. H. Fay, Brookline, Mass.
L. S. Finch, Dover, N. J.
Mrs. C. G. Fink, Yonkers, N. Y.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
Mrs. J. A. Fogarty, Berlin, N. H.
Mrs. G. S. Forbes, Cambridge, Mass.
H. F. French, Fremont, Ohio
A. P. Fuller, Niagara Falls, N. Y.
H. Gardner, New York City
C. C. Gayman, Boston, Mass.
J. W. Gibney, Buffalo, N. Y.
Mrs. H. M. Goodwin, Brookline, Mass.
N. T. Gordon, Cleveland, Ohio
Mrs. J. S. Gravely, New Haven, Conn.
J. V. Gray, Montreal, Quebec, Can.
Mrs. M. L. Griffin, North Dighton, Mass.
G. Guerner, Boston, Mass.
N. T. Hall, Cambridge, Mass.
D. Harde, New York City
S. T. Harleman, Dunkirk, N. Y.
Mrs. J. L. Harper, Niagara Falls, N. Y.
W. G. Harvey, Niagara Falls, N. Y.
R. C. Helm, Worcester, Mass.
E. Hendricks, New York City
J. Herlenius, New York City
Mrs. F. Hodson, Philadelphia, Pa.
K. Horine, Chicago, Ill.
H. E. Howe, Washington, D. C.
P. P. Hufford, Niagara Falls, N. Y.
F. D. Hupfer, Charlestown, Mass.
M. Ishizawa, New York City
H. M. Johnquest, Waterbury, Conn.
F. H. Jones, Boston, Mass.
P. T. Kaslin, Montreal, Quebec, Canada
K. Kawamote, New York City
Mrs. D. B. Keyes, New York City
R. D. Kleeman, Schenectady, N. Y.
H. S. Knowlton, Cambridge, Mass.
R. H. Lapidos, Cleveland, Ohio
S. M. Lee, Shanghai, China
C. G. Lewis, Pittsburgh, Pa.
Mrs. A. D. Little, Brookline, Mass.
R. C. McKenna, Latrobe, Pa.
M. MacFarland, Wilkinsburg, Pa.
G. H. Mains, Somerville, Mass.
R. M. Major, Bloomfield, N. J.
H. P. Martin, Niagara Falls, N. Y.
E. H. Martindale, Cleveland, Ohio
C. T. Maynard, Rumford, Me.
Mrs. D. R. Miller, Niagara Falls, N. Y.
Ruth Mott, Cleveland, Ohio
Mrs. Wm. R. Mott, Cleveland, Ohio
Mrs. J. D. Noyes, Detroit, Mich.
A. L. Pitman, Cambridge, Mass.
L. A. Pratt, Winchester, Mass.
F. H. Preble, Boston, Mass.
Mrs. H. G. Reist, Schenectady, N. Y.
W. O. Richey, New York City
W. H. Rother, Buffalo, N. Y.
W. M. Saunders, Jr., Providence, R. I.
H. R. Savage, Worcester, Mass.
I. Ichilowsky, New York City

Guests (Continued).

J. H. Schissler, Pachuca, Mexico
W. A. Selvig, Pittsburgh, Pa.
J. L. Sherrick, Arlington, N. J.
J. A. Shorey, New York City
P. B. Short, Pittsburgh, Pa.
F. D. Shumaker, Massena, N. Y.
Mrs. F. D. Shumaker, Massena, N. Y.
L. D. Simpkins, New York City
Augustus C. Smith, Buffalo, N. Y.
C. Steenstrup, Schenectady, N. Y.
A. W. Sturtevant, Lynn, Mass.
N. W. Sultzer, New York City.
M. S. Swanson, Woburn, Mass.
M. C. Tilman, Montreal, Quebec, Canada
H. G. Weidenthal, Cleveland, Ohio
H. H. Whitcomb, W. Somerville, Mass.
R. S. Williams, Cambridge, Mass.
Mrs. A. M. Williamson, Niagara Falls, N. Y.
E. D. Wooldridge, Lowell, Mass.
H. Worth, Jersey City, N. J.
G. H. Wright, Boston, Mass.
T. D. Yensen, E. Pittsburgh, Pa.
H. C. Zerr, New York City

MEMBERS ELECTED AND QUALIFIED

Since Issuing Last Membership List (January 31, 1920).

February, 1920:
A. R. DeVains
Haakon L. Ogle
J. B. Grenagle
H. F. Chappell
Clyde D. Marlatt
W. Reinders
L. R. Parker
L. L. Evans
F. F. Foss
John E. Alexander
C. E. Gibson
Etienne Caudrelier
Kenneth G. Clark
A. L. Kreiss
W. H. Falck
Guy Y. Williams
George I. Putnam
Richard K. Meade
Weston P. Demock
Harry P. Taber
Ivan P. Tashof
Frederick C. Gersen
C. W. Simmons
Harvey M. Anthony
Henry R. Schildt
Louis Schneider
J. A. Kingsbury
Robt. B. Honeyman, Jr.
F. E. Owen
John E. Weber
Leo Altenberg
Charles Wunderly
F. W. Brooke
E. A. Wilcox
F. G. Manwaring

February, 1920 (*Cont.*):
George Grumberg
D. J. Van Marle
R. A. Baxter
J. S. Hughes
Clyde F. Lyons
T. H. Cochran
D. C. Stockbarger
Geo. Janssen
H. L. Kohlberg
M. D. Mize
Harry F. Brons
Leslie S. Jenkins
W. E. McKee
R. F. Chambers
Wallace S. Chase
Ernest Moulton
Frank W. Strubing
August Herlenius
Tanizo Fukuzawa
Clarence B. Clark
Oscar A. Pickett
Louis Bernabo
W. A. Harty
Gunnar Holst
M. R. Koons
Frank B. Lounsberry
Asaka Abe
G. H. Sisson
Mathias Sem
Ed. J. Rahill
C. E. Broeker
W. A. Douglass
M. H. Kuryla
J. M. Schantz
E. H. Wellemeyer
H. W. Starr

February, 1920 (*Cont.*):
Louis W. Loncteaux
J. T. Ellsworth
James H. Bailey

March, 1920:
H. H. Foster
E. S. Alla
A. A. Rackoff
Fabian R. Staley
Robert L. Rockwell
John Cunniff
Harvey F. Mack
H. G. McIntosh
E. B. Johnson
S. R. Mason
I. F. Lancks
James B. Nicholson
Ericus Grandberg
J. W. Pugh
W. D. Pardoe
C. B. Dutton
Wm. C. Read
Myrick Crane
G. C. Dressel
Gerald G. Zeh
B. E. Field
H. T. Horn
R. A. Long
E. S. Schartzer
Robert Ammon
John T. Ott
Charles H. Fulton
E. R. Darling
F. F. Burr
C. J. Frankforter
J. E. Foglesong

Members Elected and Qualified (Continued).

March, 1920 (*Cont.*):

A. S. McDaniel
H. M. Jacoby
T. O. Westhofer
E. E. Ross
A. C. Katchman
A. J. Mandell
Birger Egeberg
Otto Maschke
John E. Esterly
Paul de Castro Maya
C. W. Ring
W. F. Rittman
Paul L. Hoover
John Disario
E. L. French
R. L. Lindstrom
Martin Hokanson
Donald S. Grenfell
Samuel J. Caplan
W. J. Fensterer
W. A. Richey
F. G. Dawson
Ovid E. Roberts, Jr.
N. Julien Thompson
Neil Hume
Geo. M. Gadsby
Robert Bishop
W. C. Dorsam
H. G. Manning
Harry Devorken
Tadashiro Incuye
Yoshio Shinjo
Shintaro Nishioka
H. A. Corliss
Walter D. Sholl
C. W. Muehlberger
J. R. Matyas
Earl H. Saunders
S. Tonami
C. A. Phillips
F. J. Metzger
Wm. Y. Bleakley
S. T. Helseth
Clarence P. Salmon
J. A. Struthers
R. R. Rees
A. W. K. Billings
E. H. French
Floyd E. Rowland
Manuel Larrea
A. E. Thurber
John H. Gardiner

April, 1920:

Geo. G. Brown, Jr.
Geo. W. Koch
L. J. Buck
Amos D. McGavy
L. P. Forman
A. R. Chamber
Michitomo Ishizawa
H. P. Bellinger
T. D. Cleage
Heihachi Kamura
Daigoro Yasukawa
Harold Roess
Fred H. Young
J. S. Guest
G. C. Lloyd
L. L. Koeper
M. C. Fleming
Henry Herman
E. Gjerding
E. Bennett
F. B. MacCarthy
John M. Wenneis
R. E. Dennis
Edmond Hutin
A. P. Champin
Tito Rondelli
R. deC. Greene
C. G. Dahlgren
Wm. Ross
H. D. Wood

May, 1920:

E. Loewenherz
Tadashiro Incuye
M. C. Beebe
Augustus Jones
H. L. Buckle
P. S. Albright
Harald Pedersen
Elbert Ross
Harry P. Fleming
John D. Toll
Benj. R. Sackett
Harold S. Booth
James Naughten
H. A. Schilling
R. T. Smith
Wm. E. Harris
C. A. Lewis
J. L. Rosenholtz
C. S. Houser
W. S. Richards

May, 1920 (*Cont.*):

S. C. Massari
Edw. E. Meisekothen
J. J. Kelly
Raymond R. Ridgway
O. A. Hougen

June, 1920:

Allen Harrison
Frank Farnsworth
H. H. Wikle
N. H. Furman
Hisao Sato
Carl Svenssen
Juichi Tanaka
A. Kenneth Graham
Jens Westly
H. M. Gassman
Junkichi Maruyama
J. W. Morris
John L. Christie
Louis Harris
W. R. Forrester
H. V. Atwell
Eric A. Arnold
C. M. Graves
T. A. Freeston
T. H. Chisholm
J. C. Downs
J. C. Dow
W. G. Harvey
A. S. Hausson
H. M. Johnquest
W. G. Berlin
R. M. Major
R. L. Baldwin
A. Aguilar
I. Kitsunezaki
L. A. Pratt
L. A. Danse
H. M. Sternfels
B. A. Stimmel
P. P. Alexander
Elmer R. Coe
Wallace G. Imhoff
W. R. Offerhans
James A. Aupperle

July, 1920:

Jen Chow
John Sissener
C. M. Eggman
W. L. Reinhardt

Members Elected and Qualified (Continued).

July, 1920 (*Cont.*):
H. E. Hineline
M. Shimada
Philip G. Deuchler
Gunnar Schjelderup
Ernest Kaufman
Bernard Price
J. B. Maneckji
C. T. Fleckenstein
Thomas S. Curtis
N. L. Leek
O. A. Knight
James B. Neal
E. L. Hix
Dott. Livio Cambi
Gerard de Geer
G. K. Paton
Susumo Fumoto
C. H. Halldin
I. C. Emery
A. F. Braid
J. F. G. Hicks
Peter Brodal
Charles G. Birdsall
H. S. Curtis
Iso Yamamoto
Alfred D. Bauer
C. H. Carpenter
Wm. Rafn
Fred H. Hotchkiss
R. H. Lapidos
Arthur W. Forsyth
Franklin Lang

August, 1920:
August Kuhlman
H. H. Blouch
Karl Horine
J. C. Broadmax
G. P. Lewis
J. W. Reno
A. J. Moxham
Allan W. Rowe
L. Eknes
R. W. Ensign
J. H. Calbeck
Yoshio Nakano
Keiichiro Asano
J. M. Nairn
Fred T. Newport
Arthur C. Carlton
C. A. Hoag
Carlos Lehmkuhl
Udaondo
S. H. Lewis
Knud Baarsrud
Henry A. de Fries
Leone Levi Bianchini
L. B. Green

September, 1920:
G. C. Klug
L. E. Wright
J. Morton Gregg, Jr.
Teizo Isshiki
Henry A. Wagner

September, 1920 (*Cont.*)
Paul F. Mumma
E. J. Kearns
E. C. Frank
Y. Horibe
Akira Kumami
Wm. W. Atkinson

October, 1920:
L. O. Grondahl
H. R. Waddell
F. C. Loh
Jackson R. Schonberg
W. L. Jordon
C. W. Bates
L. H. Reyerson
Paul D. Merica
K. Taniguchi
A. Victor Leggo
Carl Fineman
A. F. Bang
Jose B. Granell
J. R. Fuller

November, 1920:
Marion Eppley
J. K. Nulsen
W. Bartlett Jones
E. T. Moore
F. P. Case
H. C. Zen

The Presidential Address presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920.

CONTACT CATALYSIS.[1]

By WILDER D. BANCROFT.[2]

ABSTRACT.

A discussion of the present aspects of contact catalysis theory, such as whether the catalytic agent can act at a distance, by radiation, as in photochemical action, the influence of agents which retard the reacting substances from reaching the catalytic surface, the adsorption explanation of the "poisoning" of catalytic agents, the influence of change in "chemical resistance" on reaction velocity, influence of gas layers and gas bubbles, temperature coefficient, the theory of "force lines," Langmuir's theory of unsaturated valencies and atomic structure as applied to the problem.

[J. W. R.]

It seems probable that progress in developing a theory of contact catalysis can be accelerated if we formulate more definitely the conditions of the problem, so that we can see what experiments should be done next. The first question to be answered is whether the catalytic agent can act at a distance by radiation. Miss Woker[3] has given a sketch of the earlier speculations as to radiation. The only one which has survived is that of Barendrecht,[4] whose calculations have been criticized severely by Henri.[5] Trautz and Krüger[6] have attempted to account for a number of phenomena in homogeneous solutions by postulating infra-red radiation. This idea has been developed by Lewis[7] and applied to the change or reaction velocity with the temperature and to contact catalysis.

[1] Manuscript received February 22, 1920.

[2] Professor of Physical Chemistry, Cornell University.

[3] Die Katalyse (1910), 60.

[4] Zeit. phys. Chem. (1904), **49**, 456; (1906), **54**, 307; Proc. Kon Akad. Wet. Amsterdam (1919), **22**, 29.

[5] Zeit. phys. Chem. (1905), **51**, 19.

[6] Zeit. Electrochemie (1911), **17**, 453.

[7] Jour. Chem. Soc. (1914), **105**, 2330; (1915), **107**, 233; (1911), **109**, 55, 67, 796; (1917), **111**, 457, 1086; (1918), **113**, 471; (1919), **115**, 182; System of Physical Chemistry (1919), **3**, 138.

"Photochemical phenomena have demonstrated the fact that chemical change can be brought about as a result of absorption of radiation in the short-wave region. We are led to generalize this and to seek in radiation of longer wave-length the ultimate cause of ordinary or thermal reactions as well. It is obvious that every material system, in virtue of its temperature, contains radiation at the same temperature. Under ordinary conditions, *i. e.*, at ordinary temperatures, this radiation is mainly of the infra-red type. It is well known that electro-magnetic properties of substances, *e. g.*, the dielectric constant, are intimately connected with the radiation density in the material, and further, such properties have a marked effect upon the chemical activity of molecules, *e. g.*, the electrolytic dissociating power of solvents which possess high dielectric constants. It will be readily accepted, therefore, that infra-red radiation is the source of the energy which is required to bring about ordinary or thermal reactions."

By thermal reactions Lewis means reactions of the ordinary kind which proceed without being exposed to any definite external source of short-wave radiation such as is met with in the so-called photochemical reactions.

"For our present purpose the most significant phenomenon associated with thermal reactions is the influence of temperature upon the reaction velocity, the velocity constant increasing three or four fold for a rise of 10° in the neighborhood of room temperature. It has long been known that this very great effect cannot be accounted for simply on the basis of an increase in the kinetic energy of translation of the molecule as a whole, for in the most favorable case, this increase could not account for more than one or two percent of the observed effect, and it is doubtful whether the change so observed would be even in the right direction. It is evident, therefore, that the effect of temperature upon the velocity constant has to do not with the kinetic energy of translation but with the internal energy of the molecule.

"From measurements of the specific heat it is known that, on the average, the increase in the internal energy per degree rise in temperature is not large. In the simplest cases the increase in internal energy varies directly as the absolute temperature, and hence a rise of 10° would cause an increase of approximately three percent in the average internal energy at ordinary

temperatures. The influence of temperature on velocity cannot be ascribed therefore to the average increase in internal energy. When heat is added to a body, however, the energy does not distribute itself evenly among the molecules; instead, some receive no energy, others a moderate amount, and a very few receive excessively great amounts of energy. It would seem therefore that the influence of temperature on reaction-speed is to be sought in the fact that a very small number of molecules receive an abnormally large quantity of internal energy.

"By treating the problem of reaction velocity from the point of view of statistical mechanics it is possible to correlate the velocity constant with the temperature as has been done by Marcelin[8] and later in a more exact manner by J. Rice.[9] The relation between the observed velocity constant k and the absolute temperature T for a simple type of gaseous reaction is shown by Rice to be

$$d \log k/d T = E/RT^2$$

This expression is, as a matter of fact, a slightly simplified form, a small term having been neglected. In deducing this expression it has been assumed that a molecule reacts when its internal energy has been raised to a certain critical value which is in general large compared with the average internal energy of the molecule. This critical limit is known as the critical energy of the molecule. The term E denotes the difference between the critical energy and the average or mean internal energy reckoned per gram-molecule. E may therefore be called the critical increment; E denotes the amount of energy which has to be added to make an average gram-molecule react. It is at this point that the radiation hypothesis of chemical reactivity enters, the assumption being that the quantity E is contributed by the absorption of infra-red radiation of a given frequency which the substance is capable of absorbing. It is assumed that this energy is communicated in terms of quanta, the same assumption as is made by Einstein in obtaining his expression for the photochemical equivalent.

"It will be observed that the Marcelin-Rice equation is identical in form with the empirical equation of Arrhenius, which is known to be in good agreement with experiment. A considerable advance

[8] Comptes rendus (1914), 158, 161.
[9] Brit. Ass. Rep., 1915, 397.

has been made, however, in that the empirical term A, which occurs in Arrhenius' equation, is now replaced by the term E to which a definite physical significance can be attached. In the case of polymolecular reactions the active molecular state actually exists, as is shown by the experiments of Baly and F. O. Rice,[10] the rate of observed chemical reaction depends then upon the frequency of collision between activated molecules.

"In the case of unimolecular change, molecules in the active state do not exist, for it is assumed that when a molecule becomes active it immediately decomposes and becomes transformed into resultant. If the action be reversible, it follows, on the statistical basis of the expression, that the activated resultant has exactly the same critical energy as the activated reactant. This does not mean that the E term is the same for both reactant and resultant, E being the difference between the critical and mean internal energies.

"Granted that the critical increment is due to radiation, and further assuming that a single quantum is capable for accounting for the E of a single molecule, it can easily be shown from a knowledge of the magnitude of the temperature coefficient of a reaction, that the effective radiation must belong to the short infra-red region, *i. e.*, of the order 1-3 μ, in the case of reactions which occur with sensible velocity at ordinary temperatures."

In order to apply this hypothesis to contact catalysis it is only necessary to postulate that the catalytic agent emits a suitable infra-red radiation, that the sum of the critical energy increments necessary to activate the reactants at the surface of the catalytic material and the energy necessary to adsorb the products of the reaction are less than those required to activate the reactants in the free state.

Lewis[11] has done some remarkable work in the way of calculating absorption bands and of establishing relations between the critical energy increment and the heat of reaction; but he seems never to have shown experimentally that the reaction velocity is actually due to infra-red radiation. For instance methyl acetate has a strong absorption band between 5.8 μ and 11 μ and the hydrogen ion is supposed to emit wave-lengths over the range

[10] Jour. Chem. Soc. (1912), **101**, 1475.
[11] Jour. Chem. Soc. (1914), **105**, 230; (1916), **109**, 55; (1917), **111**, 457, 1086.

1.1-11 μ; but no attempt has been made to see whether infra-red radiations really accelerate the catalysis of methyl acetate. Lewis[12] tries to meet this objection in an interesting way. "In order that any of Planck's relations may be employed, it is essential that temperature radiation alone be considered, and further that the radiation and the matter composing the system be in temperature equilibrium. On Planck's view, the interchange between matter and radiant energy is effected through the medium of oscillators, situated in the molecules of the matter present. In the case of photochemical reactions as ordinarily carried out, the temperature of radiation is much higher than that of the system on which the radiation acts. To such cases Planck's expressions do not apply. It is necessary to emphasize this point, as it is not generally recognized that there is this fundamental difference between thermal and photochemical processes."

I am not prepared to admit the existence of this fundamental difference. While it is perfectly true that in photochemical work, the source of light is at a higher temperature than the object which reacts photochemically, that is merely an experimental convenience and not a theoretical necessity. The essential thing is to have wave-lengths which are absorbed by the reacting substance and it is immaterial how they are generated. If we could generate them mechanically at ordinary temperature, they would have the same photochemical action.

This point is not essential, however. If the catalytic action of hydrogen ion, for instance, is due to infra-red radiation, we ought to get acceleration when the hydrogen ion is in another vessel, provided the vessel and the solvent do not adsorb those particular infra-red radiations which are assumed to be effective. It is not a question of difference of temperature. In the same way, it ought not to be necessary theoretically to bring the mixture of sulphur dioxide and air in actual contact with the platinum. This would eliminate the danger of poisoning the catalytic agent. It is possible that this can be done; but I know of no experiments showing it and I am not certain that Lewis really believes that it can be done since he assumes[13] that gases are adsorbed in the atomic form and are therefore more active because the heat of

[12] *Ibid.* (1916), **109**, 796; System of Physical Chemistry (1919), **3**, 138.
[13] Lewis: Jour. Chem. Soc. (1919), **115**, 184.

dissociation may be ten times the heat of adsorption or condensation.

Lewis[14] does say: "It is evident that the optimum condition for the transfer of a quantum from a catalyst individual to a molecule of reactant occurs when the two are in contact and this according to the theory of probabilities is proportional to the product of the concentrations of the reactant and catalyst." This is taking radiation in a very narrow sense. Rideal[15] apparently agrees with Lewis and yet says that "the conception that adsorption is the primary action in all cases of heterogeneous catalysis is the viewpoint now generally adopted." I do not myself see any necessary connection between adsorption and a theory of contact catalysis based on infra-red radiations unless one is to assume explicitly that the infra-red radiations do not reach appreciably beyond the adsorption layer, in which case we are not dealing with action at a distance and it becomes impossible at present to say whether any of the effects are really due to infra-red radiation.

Until some proof is brought that a contact catalytic agent can act at a distance, we are justified in postulating that the reaction takes place in or at the surface. A corollary from this is that any substance, which cuts down the rate at which the reacting substances reach the catalytic surface[16] or which prevents them from reaching it, will decrease the reaction velocity and may destroy the catalytic action entirely. Berliner[17] has shown that traces of fatty vapors from the air or from the grease on the stop-cocks will decrease the adsorption of hydrogen by palladium from nearly nine hundred volumes practically to nothing. Faraday[18] has shown that traces of grease destroy the catalytic action of platinum on oxyhydrogen gas. De Hemptinne[19] has apparently shown that carbon monoxide cuts down the adsorption of hydrogen by palladium, though his method of presenting his results is very obscure. Lunge and Harbeck[20] found that carbon monoxide inhibits practically completely the catalytic action of platinum on

[14] Jour. Chem. Soc. (1916), **109**, 800.
[15] Trans. Am. Electrochem. Soc. (1919), **36**, 195.
[16] Taylor: Trans. Am. Electrochem. Soc. (1919), **36**, 149.
[17] Wied. Ann. (1888), **35**, 903.
[18] Experimental Researches on Electricity (1839), **1**, 185.
[19] Zeit. phys. Chem. (1898), **27**, 249.
[20] Zeit. anorg. Chem. (1898), **16**, 50.

a mixture of ethylene and hydrogen. Schönbein[21] pointed out that the hydrides of sulphur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the catalytic action of platinum on mixtures of air with hydrogen or ether. He considered that the hydride must decompose, giving rise to a solid film. This is not necessary in order to account for the phenomenon; but he seems to have been right in at least one case for Maxted[22] has found that hydrogen sulphide is decomposed by platinum black with evolution of hydrogen and that the platinum then does not adsorb hydrogen.

Langmuir[23] points out that "the action of oxygen in preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a catalytic poison. It has been shown previously[24] that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at 1500° K. is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered, then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur."

Harned[25] has shown that the rate of adsorption[26] of chlorpicrin by a charcoal which has been cleaned by washing with chlorpicrin is much greater at first than by a charcoal which has not been so cleaned although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium. Taylor points out that normally the time of contact between a gas and the solid catalytic agent is

[21] Jour. prakt. Chem. (1843), 29, 238.
[22] Jour. Chem. Soc. (1919), 115, 1050.
[23] Jour. Am. Chem. Soc. (1916), 38, 2272.
[24] *Ibid.* (1916), 38, 1145.
[25] Jour. Am. Chem. Soc. (1920), 42, 946.
[26] Taylor: Trans. Am. Electrochem. Soc. (1919), 36, 149.

extremely small and consequently anything which decreases the rate of adsorption will cut down the reaction velocity very much.

It is easy to see that the piling up of the reaction products will cut down the reaction velocity, if they prevent the reacting substances from coming in contact with the catalytic agent. This has been observed in the contact sulphuric acid process.[27] The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink,[28] who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperature, Henry[29] recognized that the presence of the reaction product might slow up the rate of reaction and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks the catalytic dehydration of ether[30] and of alcohol[31] and hydrogen cuts down the catalytic dehydrogenation of alcohol.

W. C. McC. Lewis[32] points out that the explanation of the poisoning of catalytic agents on the basis of adsorption leads to certain conclusions in regard to the temperature co-efficient. "One of the chief difficulties met with in the kinetics of heterogeneous reactions has its origin in the selective nature of the adsorbability of the reactants and the resultants, particularly the latter. The so-called catalytic poisons are now generally regarded as owing their effect to marked selective adsorption, as a result of which the surface of the catalyst becomes covered with a layer of molecules and is thus no longer capable of catalyzing the reaction. In many cases the resultants of the reaction are adsorbed in this manner and consequently function as a catalytic poison. Since the extent of adsorption diminishes as the temperature rises, it is obvious that when such poisoning effects are present, the temperature co-efficient of the reaction velocity over a certain range of temperature is not comparable with that over a different range, for the total observed velocity depends not only on the true effect of temperature on the chemical process, itself, but likewise on the

[27] Bodländer and Koppen: Zeit. Elektrochemie (1903), 9, 566; Beil: Zeit. anorg. Chem. (1905), 44, 267.
[28] Bodenstein and Fink: Zeit. phys. Chem. (1907), 60, 61.
[29] Phil. Mag. (1836), (3), 9, 324.
[30] Ipatieff: Ber. deutsch. chem. Ges. (1904), 37, 2996.
[31] Engelder: Jour. Phys. Chem. (1917), 21, 676.
[32] Jour. Chem. Soc. (1919), 115, 182.

alteration in the extent of active surface presented to the reactants. The simplest conditions are obviously those in which the adsorption effects are a minimum, and such conditions will occur generally when the energy required for sublimation or desorption is small. In the other cases, where adsorption effects are large, it is necessary to correct the observed velocity constants for the change in the area of the effective surface produced as a result of the change in temperature. Thus in the case in which the resultant is markedly adsorbed, and therefore acts as a negative catalyist, the temperature co-efficient will possess too high a value and, instead of decreasing as temperature rises, may even increase. A similar abnormal behavior is to be anticipated when a reaction proceeds partly in the homogeneous gaseous phase, partly in the surface, for, as the temperature rises, the reaction tends to predominate in the gaseous phase, and therefore possesses a higher temperature co-efficient."

We have seen that the poisoning of a catalytic agent is due to marked adsorption, which cuts down the adsorption of the reacting substances. We have also seen that the presence of sulphur trioxide tends to decrease the rate of reaction of sulphur dioxide and oxygen. We can now imagine a hypothetical case in which one of the reaction products is adsorbed so strongly that it acts as a poison. In that case we shall get entirely different results depending on the amount of catalytic agent present. If there is a large excess of catalytic agent the reaction will run to an end or to true equilibrium before the catalytic agent is entirely poisoned. If, on the other hand, there is only a small amount of catalytic agent, it will be poisoned very early in the course of the reaction and we shall have an apparent equilibrium reached from only one side which will vary with the amount of catalytic agent. For any given amount of catalytic agent we shall get an apparently definite end-point; but the value of the end-point will vary with the amount of catalytic agent taken. At least one case of this sort has been recognized definitely. Neilson[88] has studied the splitting of salicin and of amygdalin by platinum black. "It is found that the amount of splitting of salicin in a given time reached a maximum, and then with increasing time the amount of splitting was not proportional to the time, being materially less

[88] Am. Jour. Physiology (1906), 15, 148

in the last twenty-four hours than it was in the preceding. This is due, no doubt, to the effect of the products of the splitting—especially the saligenin. It is more probably due, however, to the salicylic acid produced by the oxidation of saligenin to salicylic acid by the platinum. It is well known that salicylic acid has a marked retarding action on enzymes as shown by Kastle and Loevenhart[34] in its action on lipase; and by Neilson[35] in its action on platinum black in the hydrolysis of ethyl butyrate.

"The experiments with amygdalin and platinum black were carried out in the same way as those with salicin. It was anticipated, however, that the amount of splitting by the action of platinum black on the amygdalin would be small, as it is well known from Bredig's work on the catalysis of hydrogen peroxide by colloidal platinum,[36] and from Neilson's work[37] on the hydrolysis of ethyl butyrate by platinum black, that hydrocyanic acid has a marked retarding action on the catalytic action of platinum. One of the splitting products of amygdalin is hydrocyanic acid; and according to the above experiments one would expect the action of platinum black on amygdalin to be retarded, if not stopped entirely. Such, indeed, was found to be the case, as the first experiment with tightly corked flasks was entirely negative. It occurred to me that by leaving the flasks uncorked the hydrocyanic acid would volatilize and the action would then proceed. This is in keeping with the well-known fact that removing one of the products of a chemical reaction allows the action to go on to completion. By leaving the flasks uncorked it was found by a qualitative test that platinum splits up the amygdalin. It was further seen that the action did not go on to completion, as the amount of sugar produced was small."

Since enzymes are poisoned by many substances in something the same way that colloidal platinum is, it seems worth while to see whether autotoxic catalysis would account for some of the peculiarities in enzyme action which have puzzled people. If autotoxic catalysis occurs, we should expect that the presence of the reaction products would cut down the reaction velocity even though the reverse reactions were negligible. If the poisoning

[34] Am. Chem. Jour. (1900), 24, 491.
[35] Am. Jour. Physiology (1903), 10, 197.
[36] Bredig: Anorganische Fermente (1900), 68.
[37] Neilson: Am. Jour. Physiology (1903), 10, 197.

action of the reaction products is sufficient, we should get false equilibria if we started with small amounts of the enzymes and the reaction would run to an end if we took larger amounts of the enzymes. Both these phenomena have been observed.[38]

The poisoning of colloidal platinum in its action on hydrogen peroxide solutions is undoubtedly due to adsorption; but we have no direct measurements on the adsorption and consequently we do not know positively that this is the right explanation and we do not know that there may not be other factors which have been overlooked.

Since reaction velocity is probably directly proportional to the difference of chemical potential and inversely proportional to the chemical resistance, we can increase the reaction velocity either by increasing the difference of chemical potential or by decreasing the chemical resistance. When the reacting substances are adsorbed at the surface of a catalytic agent, there is a marked increase in the concentration and it has been suggested that this is the cause of catalytic action. As a matter of fact, the effect of concentration seems to be relatively unimportant in most of the cases studied hitherto. Patrick's silica gel has a surface of 2.5 x 10^6 cm^2 per gram and is an excellent adsorbent; but, so far, it does not have any marked catalytic effect except in the oxidation of nitric oxide. It would be interesting to try this substance at 100° with the mixed vapors of alcohol and acetic acid, because this reaction takes place at a measurable rate in the vapor phase in the absence of any catalytic agent. It is stated that oxyhydrogen gas has been found to be quite stable under pressures of two thousand atmospheres, which shows that the catalytic action of platinum on mixtures of hydrogen and oxygen must be due to something more than a change in concentration. The marked difference in the behavior of platinum and charcoal toward oxyhydrogen gas is another argument in favor of the action of a catalytic agent being specific.

If we have selective adsorption of the reaction products, this will cause a lowering of the chemical potential of the resultants[39] and will therefore increase the reaction velocity. It may even

[38] Tammann: Zeit. phys. Chem. (1895), 18 426; Kastle and Loevenhart: Am. Chem. Jour. (1900), 24, 491.

[39] W. C. McC. Lewis suggests the terms reactants and resultants for reacting substances and reaction products.

determine the direction of the reaction. Alcohol breaks down into acetaldehyde and hydrogen in presence of pulverulent nickel and into ethylene and water in presence of pulverulent alumina. Since nickel adsorbs hydrogen strongly and alumina adsorbs water, it seems natural to assume that the selective adsorption is the determining factor.[40]

While this seems very satisfactory, there are certain points which must not be overlooked. When making ethylene at Edgewood Arsenal during the war, it was found advisable to have a large amount of steam present with the alcohol vapor in order to make temperature regulation easier. This undoubtedly decreased the rate of decomposition of the alcohol; but that difficulty was overcome by working at a higher temperature. I find it very difficult to see how alumina can dehydrate alcohol in presence of a large amount of water vapor if the reason the alumina acts is because of its strong adsorption of water vapor. In spite of the fact that the selective adsorption of the reaction products is my own pet theory and in spite of the fact that it undoubtedly contains a great amount of truth, it must be admitted that, as now formulated, it is not the final word. It must be modified before it can be considered as satisfactory. If it breaks down temporarily in the simple case of the decomposition of alcohol, it is not surprising that we cannot as yet predict the decompositions of the esters by means of it.

If changes in the chemical potential are not the important factors in contact catalysis, the catalytic agent must change the chemical resistance in some way. So far as I can see, there are two possible ways in which this might happen. We may have more effective collisions between existing molecules or we may have a conversion of one or more of the reacting substances into an active form.

According to the kinetic theory the reaction velocity is proportional to the number of collisions between possibly reacting molecules; but it does not follow at all that two molecules react every time they collide. If a large number of collisions is necessary on an average before a pair of molecules react, anything which would make these collisions more helpful might increase the reaction velocity enormously. The first question is then whether

[40] Bancroft: Jour. Phys. Chem. (1917), 21, 591.

there is any evidence of ineffective collisions. This matter has been studied by Strutt,[41] who comes to the conclusion that a molecule of ozone reacts every time it strikes a molecule of silver oxide; but that a molecule of active nitrogen collides with a molecule of copper oxide five hundred times on an average before they react, while two molecules of ozone at 100° collide on an average 6 x 10″ times before they react. Without insisting on the absolute accuracy of these figures there is evidently plenty of margin for an increase in reaction velocity with ozone at 100° if one could produce more effective collisions. Langmuir[42] finds that 15 percent of all oxygen molecules at a pressure of not over 5 bars striking a tungsten filament at 2770° K react with it to form tungstic oxide, WO_3. This co-efficient increases at higher temperatures and at 3300° K about 50 percent of all the oxygen molecules which strike the filament react with it to form WO_3. Since there are three atoms of oxygen in WO_3 and only two in the oxygen molecule, Langmuir considers that at least one-half of the tungsten surface must be covered at 3300° K with oxygen in some form.

It is possible that a catalytic agent may cause one molecule to strike another amidships instead of head-on and may thereby increase the effectiveness of the collisions. It is not impossible that part at least of the effect of solvents on reaction velocity may be due to some such thing as this. If we adopt Langmuir's views of oriented adsorption, all sorts of things become possible. If ethyl acetate, for instance, attaches itself to one adsorbent by the methyl group, to another by the ethyl group, and to a third by the carboxyl group, it might very well be that bombardment of the captive molecule by free ones might lead to very different reaction products in the three cases. Such a suggestion is of very little value, however, unless it can be made definite. We do not know as yet whether ethyl acetate is actually adsorbed in one way by nickel, in another way by thoria, and in a third way by titania, nor do we know whether the difference in the manner of adsorption, assuming it to occur, is of such a nature as to account for the differences in the reaction products. It may well be that some entirely different hypothesis will prove necessary. The general

[41] Proc. Roy. Soc. (1912), 87, A, 302.
[42] Jour. Am. Chem. Soc. (1913), 35, 105; (1916), 38, 2270.

problem of increasing the effectiveness of molecular collisions is distinctly an important one which has not been studied at all.

There is one special case in which we can apparently identify one of the factors of chemical resistance. Buchböck[43] studied the decomposition of carbonyl sulphide and found that the reaction velocity decreased with increasing viscosity of the solution. Since the reaction products are gases, this suggests the possibility that the retardation is due to the greater difficulty of forming gas bubbles in a more viscous medium. This receives confirmation from Raschig's work on the preparation of hydrazine.[44]

"The best method for the preparation of hydrazine is that discovered by Raschig. His original process[45] consisted in treating a solution of hypochlorite with excess of ammonia in the cold and then heating the mixture, with the result that the monochloroamine first formed interacted with the excess of ammonia to produce hydrazine. For example, one liter of a solution of sodium hypochlorite containing about 70 grams of active chlorine is added to one liter of a 20 percent solution of ammonia, the temperature being kept below 15°. The mixture is without delay heated to boiling, and by boiling off the excess of ammonia, acidifying with sulphuric acid and evaporating to crystallization the hydrazine is isolated as the sparingly soluble sulphate. The yield is about 25 percent of the theoretical quantity.

"In the first stage of the process monochloroamine is formed by interaction of the hypochlorite and the ammonia:

$$NH_3 + NaOCl = NH_2Cl + NaOH.$$

The chloroamine in turn may react with the ammonia either (1) with liberation of nitrogen and formation of ammonium chloride:

$$3NH_2Cl + 2NH_3 = N_2 + 3NH_4Cl,$$

or (2) with the production of hydrazine hydrochloride:

$$NH_2Cl + NH_3 = N_2H_4HCl,$$

and the success of the method, so far as the preparation of hydrazine is concerned, depends upon increasing the velocity of the

[43] Zeit. phys. Chem. (1897), 23, 123; (1900), 34, 229.
[44] Henderson: Catalysis in Industrial Chemistry (1919), 60.
[45] Eng. P. (1907), 22957.

second reaction or retarding that of the first. It has been found[46] that the addition to the mixture of certain liquids thicker than water increases the yields of hydrazine to between 40 and 50 percent of the theoretical; such liquids as 5 percent solutions of cane sugar, glycerol, dextrin, or starch are suitable for this purpose. Yields of from 60 to 80 percent of the theoretical may be obtained by adding solutions of gelatine, albumin, casein, etc., to a mixture of nine parts of a concentrated solution of ammonia and one part of a solution of a hypochlorite containing about 70 grams of active chlorine per liter."

Henderson uses the word "thicker" where most of us would say "more viscous," as is shown by another account of Raschig's results.[47] It is very desirable that experiments be made with other reactions involving the evolution of gas, such as the decomposition of the diazo-compounds[48] for instance, so as to make certain that this phenomenon is a general one.

Instead of more effective collisions between unchanged portions of the reacting molecules we may have a partial conversion of one or more of the reacting substances into active forms either through the rupture of normal valences or of contra-valences, opening up fields of force, as Baly puts it.

In order to account for the change of reaction velocity with change of temperature in the case of such reactions as the inversion of cane sugar, Arrhenius[49] fell back on the hypothesis which had developed into the electrolytic dissociation theory and postulated the existence of active and inactive molecules of cane sugar. If the number of active molecules is very small relative to the inactive ones, a slight displacement of the equilibrium would account for a large percentage increase in the reaction velocity. This hypothesis did not prove fruitful and no progress was made in determining what was the difference between the active and inactive molecules. Since the majority of reactions have temperature co-efficients larger than can be accounted for on the kinetic theory, this meant that practically all substances occurred in two

[46] Eng. P. (1908), 139.

[47] Woker: Die Katalyse (1910), 194.

[48] Hausser and Müller: Comptes rendus (1890), 114, 549, 667, 760, 1438; Bull. Soc. chim. Paris. (1892), (3), 7, 721; (1893), 9, 353; Hantzsch: Ber. deutsch. chem. Ges. (1902), 33, 2517; Cain and Nicoll: Jour. Chem. Soc. (1902), 81, 1412; (1903), 83, 206; Bredig and Fraenkel: Zeit. Elektrochemie (1905), 11, 525; Fraenkel: Zeit. phys. Chem. (1907), 60, 202.

[49] Zeit. phys. Chem. (1889), 4, 226.

forms, the active form always being relatively low in concentration. This was so unsatisfactory that most persons have preferred to accept the temperature co-efficient as an empirical fact without attempting any theoretical explanation.

W. C. McC. Lewis[60] comments as follows on this hypothesis of Arrhenius: "The principal criticism of the concept of active and passive molecules, having a real existence and existing in mass action equilibrium with each other, enters when the concept is extended to account for the catalytic influence of say $H^{\cdot}$ ions or other solutes, a subject which will be discussed in the next section. The concept of active and passive molecules has in fact been applied to cases of catalysis, the idea being that a catalyst, such as $H^{\cdot}$ ion, acts as an accelerator in virtue of the effect which it exerts on the number of active molecules, increasing these to a considerable extent, and thereby hastening the reaction. If this were true, we would have a case in which the equilibrium constant, X, was altered, and altered very considerably, by the presence of a dissolved catalyst. This is contrary to all experience in those cases in which equilibrium constants can be measured. It is therefore too uncertain to be accepted in a case in which we are unable to verify it experimentally. That mixed solvents, *i. e.*, the addition of a considerable quantity of one solvent to another, can bring about a shift of the equilibrium constant is known; we have already discussed such a case in connection with Godlewski's determination of the Ostwald constant for certain weak acids in alcohol-water mixtures. This is, however, quite a different state of affairs from that represented by the addition of say $H^{\cdot}$ ions (in the form of an acid) in quite small quantities, so small, in fact, that the properties of the medium are only slightly altered.

"As a matter of fact, it is quite possible to account not only for the marked effect of temperature in the case of a monomolecular reaction, but also for the effect of catalysts, on a purely physical basis, which does not require any explicit assumption regarding the equilibrium between active and passive molecules, but simply deals with the problem from the standpoint of the internal energy of the molecules and the statistical distribution of this internal energy."

[60] System of Physical Chemistry (1918), 1, 413.

Baly and Krulla[51] consider that the change to an active form consists in opening the condensed systems of force lines. "Although the term residual affinity has frequently been used to explain many chemical processes, no satisfactory and connected explanation has been brought forward as to the nature and origin of this property. It is generally accepted that the formation of compounds such as hydrates and double salts are due to the secondary valencies of the atoms of the compounds concerned, and that every elementary atom possesses these secondary valencies to a greater or lesser extent. In any compound that is formed by virtue of the primary valencies of its atoms only, the secondary valencies are unsatisfied or unsaturated. Every atom must therefore be the centre of a field of force, the nature and strength of which depends on the nature of the secondary valencies in each case. In addition to the unsaturation of the secondary valencies, we must add the unsaturation of the primary valencies, when this is known to exist. Clearly therefore such atoms in a compound must be the centre of a field of force the lines of which radiate in every direction.

"Now the independent existence of the several fields of force in any one molecule must be a metastable condition, for the lines of force of the several fields must condense together with the escape of free energy. The results of this condensation will be the production of a closed system of force lines, and the free affinities of the molecule will be considerably reduced. When the condensation of the force lines has occurred, it is not necessary that the whole of the free affinities should disappear, for this will only take place when there is a perfect equality between those of opposite type within the molecule. In those cases where there is not a perfect equality there will naturally be left a balance of affinity, and it is this balance which should be defined by the term "residual affinity," and this term should mean that amount of affinity left uncompensated after the maximum condensation between the force fields has occurred. This residual affinity of a molecule may be of positive or negative, or, as more usually called, basic or acid type, according to the conditions obtaining within the molecule.

"Again it is evident that the chemical reactivity of a molecule must depend on the free affinity which exists and it is a necessary

[51] Jour. Chem. Soc. (1912), 101, 1469.

deduction that the condensing together of the lines of force must result in a decrease of chemical reactivity, and, indeed, it would seem to follow that the true chemical reactivity of any molecule cannot be exhibited until the condensed systems of force lines within each molecule have been unlocked or opened by some means."

Baly and Rice[52] have applied this conception of condensed systems of force lines around the molecules to chemical action and to catalysis. "It is evident that the condensing together of the lines due to the force fields round the component atoms of a molecule must result in an enormous decrease in the reactivity of the molecule, and, in fact, it may be said that such a condensed system cannot react unless it previously be opened or unlocked by some means. For example, the well-known cases described by Baker, when pure, dry substances such as ammonia and hydrogen chloride, lime and carbon dioxide, do not react together are doubtless due to the fact that the force fields of the molecules are so condensed together that no reaction takes place when they are brought together. The presence of water is required in order to open these systems sufficiently for the reaction to proceed, the merest trace of water being enough to catalyze the whole reaction. Again, the converse cases of the vapors of ammonium chloride and mercurous chloride may be explained in the same way, for these molecules evidently possess their force fields so condensed that increase of temperature alone is not sufficient to open them, and the vapor densities correspond with those of the undissociated molecules. The presence of water, however, opens the condensed fields sufficiently for the molecules to dissociate under the influence of higher temperatures.

"The general phenomenon of catalysis is capable of explanation on these lines, for a catalytic agent may be defined as one which opens the condensed system of the reacting substance or substances so that their chemical reactivity is enhanced. Negative catalysis is equally capable of explanation, for a negative catalyst is simply a type of substance which tends to close up the condensed systems, and thus counteract the action of the solvent. Specific evidences of such closing of the molecular systems have been observed from absorption spectra, as will again be mentioned.

[52] Jour. Chem. Soc. (1912), 101, 1475.

"It follows from the above that any chemical reaction must take place in at least two stages. First, the reacting substances must have their condensed systems opened up, and, secondly, these opened systems will react together to give the expected compound. It is clear that these stages should be possible of observation, and that, in the event of their taking place, they should evidence themselves in some way. There is no doubt that the explanation of the color changes of the aromatic amino aldehydes and ketones when treated with alcoholic hydrogen chloride are due to these states in the reaction. When, for example, o-amino-benzaldehyde is dissolved in alcohol, the condensed system is partly opened owing to its penetration by the force lines due to the residual affinity of the alcohol. On the addition of hydrogen chloride, the final product is, of course, the hydrochloride; but the base in the form in which it exists in alcoholic solution does not itself react with the acid to give the salt. It passes through an intermediate phase when it is opened up to a more complete stage, and it is this intermediate phase that reacts with more acid to form the salt. The intermediate phase has a yellow or red color with a characteristic absorption band[83] as has already been described."

Experiments with the nitro-anisols dissolved in alcohol and in concentrated sulphuric acid showed the occurrence of a stage in the sulphuric acid solution preliminary to the sulphonation. The authors consider that this is an intermediate formation of $CH_3O\ C_6H_5.H_2SO_4$. They consider that any molecular transformation whatsoever may be looked upon simply as a re-arrangement of the electrons due to the potential gradient within the condensed systems of force lines of the molecule being sufficiently steep.

In a discussion of catalysis in homogeneous systems, Dhar[84] says: "If active and inactive molecules exist, it appears reasonable to expect that a catalyst or light simply acts in shifting this equilibrium. Plainly if sufficient catalyst were added to change a relatively large amount of inactive into active molecules or *vice versa*, it would follow that the temperature co-efficient would be smaller than that when the reaction is not catalyzed." This proved to be true experimentally. In the oxidation of quinine sulphate

[83] Baly and Marsden: Jour. Chem. Soc. (1908), 93, 2108.
[84] Jour. Chem. Soc. (1917), 111, 746.

by chromic acid the temperature co-efficient is 1.87 in the dark and 1.04 in the light. With iodine and potassium oxalate, the temperature co-efficient is 6.73 in the dark and 3.4 in diffused light. Mercuric chloride and potassium oxalate showed a temperature co-efficient of 2.2 in the dark and 1.19 in the light.

If a contact catalytic agent is to increase the relative amounts of the active molecules, it must displace the equilibrium. This presents no difficulty if one considers the catalytic agent as acting in some respects like a solvent.[55] or if one considers it as acting by radiation.[56]

The conception of Baly that a catalytic agent activates the reacting substances by opening up fields of force covers the ground admirably as a purely formal statement. The trouble with it is that it is as yet too vague to be of any value as a working hypothesis, though it is undoubtedly the best starting point. It is necessary to show in each particular case just what happens and why it happens. While the conversion of a reacting substance into an active form may very well account for the effect of the solvent on reaction velocity in homogeneous systems, it must be shown what active form is produced and why one solvent produces more of it than another. Activation may lead to the formation of intermediate compounds or it may not; but we have got to get down to more definiteness in all the cases of contact catalysis. It is often assumed that definite intermediate compounds are formed and this is certainly true in some cases. In the catalysis of hydrogen peroxide by mercury, the intermediate formation of mercuric peroxide can be detected by the eye because there is an intermittent formation of a film, which then breaks down, only to form again.[57] The formation of graphite is usually preceded by the formation of a carbide. The conversion of acetic acid into acetone[58] by passing the vapor over heated barium carbonate presumably involves the intermediate formation of barium acetate, though one cannot ear-mark the carbon dioxide and so cannot be absolutely certain that the barium carbonate is continually decomposed and regenerated. In the Deacon chlorine process, where a

[55] Bancroft: Jour. Phys. Chem. (1917), 21, 588.

[56] Lewis: Jour. Chem. Soc. (1919), 115, 182.

[57] Bredig and von Antropow: Zeit. Elektrochemie (1906), 12, 581; von Antropoff: Jour. prakt. Chem. (1908), (2), 77, 273.

[58] Squibb: Jour. Am. Chem. Soc. (1895), 17, 187.

mixture of hydrochloric acid and oxygen are passed over heated cupric chloride, Hurter[59] assumes the existence of an intermediate compound. People are not agreed, however, whether the intermediate compound is cuprous chloride, cupric oxychloride, or both. The extreme sensitiveness of this reaction to poisons raises a question whether an intermediate compound really is formed. In the catalytic oxidation of carbon monoxide, it is usually believed that there is alternate reduction and oxidation of the oxides which act as catalytic agents.

Sabatier[60] believes that the catalytic action of alumina on alcohol is due to the intermediate formation of an unstable compound of alumina and water. On the other hand, Henderson[61] assumes the intermediate formation of aluminum ethylate. Neither man offers any experimental evidence in support of his belief, and neither one discusses why kaolin should act practically as well as alumina.

Langmuir[62] considers that the particles of a crystal of any solid mass are held together by chemical forces and therefore constitute a giant molecule. An adsorbed gas will be held chemically by the unsaturated valences at the surface of the solid. "In general the law of multiple combining proportions will apply. Thus each metal atom of the surface will be capable of holding a definite integral number (such as one or two) of atoms of the gas or possibly each two atoms of metal may hold one atom of gas. The atoms held on the surface in this way will form a part of the solid body, being a real continuation of the space lattice of the solid. This layer of atoms (or molecules) on the surface may be said to be adsorbed. The surface of the metal is thus looked upon as a sort of checker-board containing a definite number N_0 of spaces per square centimeter. The number of elementary spaces, N_0, is probably usually equal to the number of metal atoms on the surface. But this is not essential, for we can imagine cases in which each metal atom holds for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface."

These so-called compounds are not of the ordinary type and no definite formulas can be written for them. In the case of the

[59] Jour. Soc. Chem. Ind. (1883), 2, 106.
[60] Die Katalyse in der organischen Chemie (1914), 240.
[61] Catalysis in Industrial Chemistry (1919), 4.
[62] Jour. Am. Chem. Soc. (1915), 37, 1139; (1916), 38, 1145.

adsorption of argon by charcoal, we should have to write C_xAr_y, where x varies with the mass of the charcoal and y with its surface and also with the pressure and temperature. I have therefore called these substances indefinite intermediate compounds.

Starting from this point of view, Langmuir[63] has developed a theory of contact catalysis, which however deals primarily with the form of the reaction velocity equations and does not throw much light on the real problem of contact catalysis. This defect could be remedied if the theory were developed to such an extent as to show that an ester was adsorbed in different ways by different catalytic agents and that the reaction took place at the point in the molecule where the ester tied on to the adsorbent forming the indefinite compound. This is a perfectly normal development because Langmuir now postulates that hydrogen is taken up as monatomic and not as molecular hydrogen.

In so far as an adsorbing agent acts like a solvent, it may open up fields of force without necessarily postulating the formation of definite or indefinite compounds. The same criticism applies to this as to the others. We must devise some method of handling specific cases so that we can tell what the actual steps are in each case.

This general treatment of contact catalysis as a problem in activation has the advantage of suggesting a possible explanation for the behavior of promoters. Rideal and Taylor[64] say:

"Thus far no theory put forward to account for the acceleration of reaction by minute quantities of promoters added to the main catalyst material is completely satisfactory. A possible mechanism, which, however, has received no experimental test, may be advanced by considering the case of ammonia synthesis from mixtures of nitrogen and hydrogen. Reduced iron is an available contact substance, the activity of which may be regarded as due to the simultaneous formation of the compounds, hydride and nitride, with subsequent re-arrangement to give ammonia and unchanged iron. Or, maybe, the activity of the iron is due to simultaneous adsorption of the two gases. The particular mechanism of the catalysis is unimportant for the present considerations. Now such bodies as molybdenum, tungsten, and uranium have

[63] Jour. Am. Chem. Soc. (1916), 38, 2286.
[64] Catalysis in Theory and Practice (1919), 31.

been proposed, among others, as promoters of the activity of iron. It is conceivable that these act by adjusting the ratio in which the elementary gases are adsorbed by or temporarily combined with the catalytic material to give a ratio of reactive nitrogen and hydrogen more nearly that required for the synthesis, namely, one of nitrogen to three of hydrogen. From the nature of the materials suggested as promoters, it would seem that they are in the main nitride-forming materials, which on the above assumption of mechanism would lead to the conclusion that the original iron tended to adsorb or form an intermediate compound with a greater proportion of hydrogen to nitrogen than required by the stoichiometric ratio. The catalytic activity of reduced iron as a hydrogenation agent would tend to conform this viewpoint.

"In reference to this suggested mechanism it must be emphasized, however, that in such examples of 'promotion,' as require only minute quantities of added promoter the activity is more difficult to understand. With the case of ammonia synthesis, the promoters are added in marked concentrations. It is difficult to realize, however, that 0.5 percent of ceria or a concentration of one molecule of ceria among 200 molecules of iron oxide, in the example cited above in reference to catalytic hydrogen production, can so far 'redress the balance' of adsorption or combination as to produce the marked increase in activity of which it is capable. It is obvious that in this phase of the problem there lies an exceedingly fascinating field for scientific investigation, with the added advantages that, being practically virgin territory, the harvest to be gained therefrom should be rich and abundant."

Instead of the promoter changing the ratio of adsorption, it might be that the catalytic agent activates only one of the reacting agents or activates one chiefly, and that the promoter activates the other. Thus it might be, in the ammonia synthesis, that iron activates the hydrogen chiefly so that we have hydrogenation of the nitrogen. The molybdenum might tend to activate the nitrogen giving rise to nitridation of hydrogen, or it might increase the activation of the nitrogen. Such a state of things is not impossible theoretically. When a dye reacts with oxygen under the influence of light, it may be that the light makes the oxygen active and that the activated oxygen oxidizes the dye, or it may be that the light makes the dye active and that the activated dye reduces

the oxygen. It is easy to decide this question by seeing whether the effective light corresponds to an absorption band for the dye or for the oxygen.

Promoter action is by no means confined to the ammonia synthesis. Pease and Taylor[65] have collected the data on promoter action. Ipatiew[66] found that copper oxide in an iron tube was much more effective in causing the hydrogenation of amylene than was copper oxide in a copper tube. The Badische Company[67] state that hydrogenation of fats with nickel is accelerated by presence of tellurium. Dewar and Liebmann[68] claim that a mixture of nickel and copper oxides can be reduced in the oil at 190° and will hydrogenate cottonseed oil rapidly at that temperature, whereas nickel oxide alone requires a temperature of about 250° for reduction. Hochstetter[69] found that a mixture of silver and copper was more effective for the synthesis of formaldehyde from methyl alcohol than either metal singly. Maxted[70] states that bismuth, tungsten and copper make iron more active in the ammonia oxidation. Mixed oxides are more effective in the oxidation of carbon monoxide than any of the oxides taken singly. The phenomenon of promoter action is thus a fairly common one.

It seems probable that the best way to solve the problem of contact catalysis is to start with the side which has been neglected a good deal and to study the selective action of catalytic agents. Quite apart from any theory we may adopt, there are certain questions which ought to be answered experimentally and yet these questions have not even been raised in a serious way. We know that ethyl alcohol can be decomposed into acetaldehyde and hydrogen or into ethylene and water, but that is practically all that we know as yet about these reactions. With pulverulent nickel the reaction is almost completely

$$CH_3CH_2OH = CH_3CH_2O + H_2$$

We do not know whether the hydrogen comes off in one stage or in two. If it comes off in two stages, is the first stage CH_3CH_2O or $CH_3CH\,OH$? While it may not be easy to devise a method

[65] Jour. Phys. Chem. (1920), 24, —.
[66] Ber. deutsch. chem. Ges. (1910), 43, 3387.
[67] German Patent (1913), 282782.
[68] U. S. Patents, 1268692, 1275405.
[69] U. S. Patents, 1100076, 1110289.
[70] Jour. Soc. Chem. Ind. (1917), 36, 777.

which will answer this question, the problem is not more difficult than many which the organic chemists have solved successfully.

With pulverulent alumina the reaction is almost completely

$$CH_3CH_2OH = CH_2CH_2 + H_2O.$$

Does water split off as such or do we get the splitting off of hydroxyl or hydrogen? It seems improbable that water can split off as such because then it would be difficult to account for the intermediate formation of ether. If the first stage is a splitting off of hydroxyl does the other hydrogen come from the adjacent carbon atom giving ethylene direct or does it come from the same carbon atom, forming a substituted methylene, CH_3CH, which then re-arranges to ethylene. The study of contact catalysis is really bringing us back to the work of Nef, though from a somewhat different angle. Somebody will some day have to go over all the methylene chemistry of Nef, sorting out what is good and showing that it is good and why it is good. Nef refused to recognize anything except a methylene dissociation, which was an unfortunate attitude to take.

With nickel we get the following decomposition of the esters:

$$CH_3CO_2CH_2CH_3 = CH_3CH_2CH_3 + CO_2$$
$$CH_3CO_2CH_3 = CH_3CH_3 + CO_2$$
$$H\ CO_2CH_3\ (?) = CH_4 + CO_2$$

With thoria the decomposition is quite different:

$$2CH_3CO_2C_2H_5 = CH_3CO\ CH_3 + CO_2 + (C_2H_5)_2O$$
$$= CH_3CO\ CH_3 + CO_2 + C_2H_5\ OH + C_2H_4$$
$$2CH_3CO_2CH_3 = CH_3CO\ CH_3 + CO_2 + (CH_3)_2O$$
$$2H\ CO_2CH_3 = H\ CH\ O + CO_2 + (CH_3)_2O$$

With titania we have a third set of products:

$$CH_3CO_2C_2H_5 = CH_3CO_2H + C_2H_4$$
$$2CH_3CO_2CH_3 = 2CH_3CO_2H + C_2H_4$$
$$H\ CO_2CH_3 = H\ CO_2H + CH = CO + CH_3OH$$

The decompositions are regular and characteristic with each catalytic agent and the molecules must break or slip at different points in the different cases; but we certainly ought to know what

the hypothetical intermediate stages are.[71] Take the case of methyl acetate with nickel, for instance. One assumption might be that we have a methylene dissociation

$$CH_3CO_2CH_3 = CH_3CO_2H + CH_2 = CH_3CH_3 + CO_2$$

A second assumption is that methyl splits off:

$$CH_3CO_2CH_3 = CH_3CO_2 + CH_3 = C_2H_6 + CO_2$$

A third assumption might be a splitting off of both methyl groups:

$$CH_3CO_2CH_3 = 2CH_3 + CO_2 = C_2H_6 + O_2.$$

Is any of these what happens and how can we prove it? Also how does the final assumption tie in with the facts that in aqueous solution acetate ion goes to ethane and CO_2.

$$2CH_3CO_2 = C_2H_6 + 2CO_2$$

and that dry lead tetra-acetate decomposes at about 140° into lead acetate, methyl acetate and carbon dioxide

$$Pb(CH_3CO_2)_4 = Pb(CH_3CO_2)_2 + CH_3CO_2CH_3 + CO_2$$

The question also comes up as to the changes in the intermediate stages in case the esters are chlorinated more or less completely.

Another case of selective action about which we need more information is that of preferential combustion. We know[72] that at low temperatures hydrogen burns more readily than methane in presence of platinum and there is some evidence to show that the same thing is true at high temperatures. In presence of copper oxide at 250° all the hydrogen in a mixture of hydrogen and methane can be burned without any of the methane being decomposed. In presence of chamotte at 500° hydrogen burns much more readily than methane. In borosilicate glass bulbs at 300°–400°, methane is burned much more rapidly than hydrogen or carbon monoxide and the same is true when mixtures of methane and oxygen with hydrogen or carbon monoxide are exploded by a spark. We need data, however, to show just why this should be so in each case. Rideal[73] has found that in gas mixtures, con-

[71] This is now being studied experimentally by Professor Homer Adkins.
[72] Bancroft: Jour. Phys. Chem. (1918), **22**, 674.
[73] Jour. Chem. Soc. (1919), **115**, 993.

taining carbon monoxide, hydrogen and oxygen, undergoing surface combustion at the surface of various catalytic agents, the ratio of carbon monoxide to hydrogen burnt varies with the nature of the catalytic material.

Selective action may occur markedly in electrolytic processes. With different cathodes we may get different reduction products and this is due in many cases to differences of over-voltage. The most probable explanation of hydrogen over-voltage[74] is that it is due to the concentration of electrically neutral monatomic hydrogen at the cathode. The metals which have a lower over-voltage are those which catalyze the reaction $2H \rightarrow H_2$, while those which have a high over-voltage do not. This was suggested as a possible hypothesis by Ostwald[75] and by E. Müller.[76] It was brought forward seriously by Tafel[77] and was urged again by Lewis and Jackson[78] and by Brunner,[79] but only to meet special cases. Bennett emphasized the irreversibility and generalized the application. The work of Langmuir and his assistants on active hydrogen[80] gives an independent experimental confirmation which was lacking at the time Tafel and Lewis and Jackson wrote. While this seems unquestionably the true explanation of the phenomenon, it must be admitted that the details have not yet been worked out and that only recently has anything been done to bring over-voltage in line with the hydrogenation and dehydrogenation work of Sabatier. (Rideal: Jour. Am. Chem. Soc. (1920), **42**, 106).

Even in cases where the theory seems applicable, there are no new quantitative data. The rapid breaking down of sodium amalgam when certain impurities such as iron, cobalt, or nickel are present,[81] is due unquestionably to the decrease in the over-voltage, or, in other words, to the increased rate of formation of ordinary hydrogen from monatomic hydrogen.[82] It is for this reason that sodium amalgam must be made in porcelain vessels and not in iron pots or enamelled ware.[83] It seems probable that

[74] Bennett and Thompson: Jour. Phys. Chem. (1916), 20, 296; Bancroft: 396.
[75] Zeit. Elektrochemie (1889), 6, 40.
[76] Zeit. anorg. Chem. (1901), 26, 11.
[77] Zeit. phys. Chem. (1900), 34, 200; (1905), 50, 641, 713.
[78] Proc. Am. Acad., 41, 399; Zeit. phys. Chem. (1906), 56, 207.
[79] Zeit. phys. Chem. (1906), 56, 331.
[80] Langmuir: Jour. Am. Chem. Soc. (1912), 34, 860, 1310; Freeman: (1913), 35, 931; Langmuir and Mackay (1914), 36, 1708; Langmuir: (1915), 37, 417.
[81] Walker and Paterson: Trans. Am. Electrochem. Soc. (1903), 3, 185.
[82] *Cf.* Lewis and Jackson: Proc. Am. Acad. (1906), 41, 403.
[83] Baeyer: Ber. deutsch. chem. Ges. (1892), 25, 1255.

alcohol and many organic substances lower the over-voltage with sodium amalgam because Fernekes[84] found that these substances increase the rate of reaction between sodium amalgam and water; but there are no direct measurements to prove this, though Carrara[85] has shown that the over-voltage in methyl alcohol and ethyl alcohol are quite different from what they are in water. I have often wondered whether the reason that nobody has ever prepared electrolytically a sodium alloy, using a cathode of fused Wood's alloy, might not be because the over-voltage is not sufficient in this case.

While a high hydrogen over-voltage and high reducing power generally run parallel, it does not follow necessarily that all reductions will take place more readily at the cathode showing the higher over-voltage. Other factors may come in, as in the case of nitrates and nitrites. If the over-voltage were the only factor, it would not be possible for nitrates to be reduced more readily than nitrites at one cathode and less readily at another. This is the case, however.[86] At cathodes of zinc, iron, lead, platinum, and gold, nitrite is reduced the more readily. Boehringer and Sons[87] claim that with hot solutions and a mercury cathode, sodium nitrate is reduced more readily than sodium nitrite. Caffeine is reduced more readily at a mercury cathode than at a lead one,[88] while the reverse is true with succinimide. Müller[89] has called attention to a number of abnormal cases, among others to the fact that more ammonia is obtained by reducing a nitrate solution with an iron cathode than with a platinum or a zinc one, although the potential drop with the iron cathode was the lowest. Chilesotti[90] has pointed out the peculiar behavior of molybdic acid at different cathodes.

There are at least three distinct factors which may mask the relation between over-voltage and reducing power. One of the substances to be reduced may be adsorbed much more than the other, so that the effective concentration at the surface of the

[84] Jour. Phys. Chem. (1903), 7, 611.
[85] Zeit. phys. Chem. (1909), 69, 75.
[86] Müller: Zeit. anorg. Chem. (1901), 26, 1; Zeit. Elektrochemie (1903), 9, 955; (1905), 11, 509.
[87] Zeit. Elektrochemie (1906), 12, 745.
[88] Tafel and Neumann: Zeit. phys. Chem. (1915), 50, 713.
[89] Zeit. anorg. Chem. (1901), 26, 43; Zeit. Elektrochemie (1907), 13, 601; (1908), 14, 429.
[90] Zeit. Elektrochemie (1906), 12, 146, 173.

electrode may be very much higher than the mean concentration in the solution. The electrode may catalyze other reactions besides the one $2H \rightarrow H_2$. This possibility was foreseen by Ostwald[91] sixteen years ago and is apparently realized with the iron cathode in a nitrate solution because the selective adsorption of ammonia is probably the reason for the apparently abnormal result. A third possibility was pointed out to me by Mr. Bennett, that particular substances may catalyze the reaction, $2H \rightarrow H_2$, so that the overvoltage at a given cathode may vary with the nature of the apparently inert substances in the solution. We know that this happens when we add something which poisons the electrode.[92]

Taylor[93] calls attention to the fact that a given solid catalytic agent can be so activated by suitable treatment that the apparent reaction temperature may be changed several hundred degrees. "If hydrogen be passed over the copper oxide wire of commerce, rapid reduction begins in the neighborhood of 300°. If the copper so formed be oxidized at a somewhat lower temperature it will be found that subsequent rapid reduction will occur at a lower temperature than in the first reduction. This process of oxidation can be repeated to such a degree that the wire becomes sufficiently reactive to be reduced or oxidized at 100°; and examination of the wire shows that it is in a similar physical condition to that of the activated platinum [used in the ammonia oxidation.] Such copper oxide, moreover, will catalyze rapidly the combination of hydrogen and oxygen at 100°, whereas charcoal will be inert. We see therefore that in increasing the chemical reactivity of the contact agent we have increased its catalytic activity. Now the results thus obtained by careful preparation of the catalyst in a highly reactive state with simultaneous variation of its physical characteristics are frequently produced more readily by the use of promoters. Normally it would be anticipated that the catalytic activity of a mixture should be composite of the several activities of the components and such is of very frequent occurrence. Nevertheless exceptions are well known and it has often been shown that the admixture of small quantities of other substances with single catalysts results in an abnormal increase in the cata-

[91] Trans. Am. Electrochem. Soc. (1904), 6 II, 187.
[92] *Cf.* Reichinstein: Zeit. Elektrochemie (1910), 16, 297.
[93] Trans. Am. Electrochem. Soc. (1919), 36, —.

lytic activity of the mixture. Thus a mixture containing 2.5 percent Cr_2O_3 and 0.5 percent CeO_2 with iron oxide gives a catalytic agent for the interaction of stearin and carbon monoxide many times more reactive than iron oxide alone unless this latter is submitted to exceedingly careful treatment. To such admixtures the name of catalyst promoters has been given. As yet the explanation of promoter action is not forthcoming. Indeed it is probable that no one single theory would be generally applicable in certain cases, as for example in the use of molybdenum as a promoter of iron in ammonia synthesis, the phenomenon may be associated with the nitride-forming or nitrogen-adsorbing properties of molybdenum. In cases of carrier action, as for example in oxidation processes, where catalytic action may possibly be associated with the tendency of an element to oscillate between two stages of oxidation, the function of the promoter may be to increase the temperature range over which the catalytic agent is labile. It would seem in other cases that promoters may act by decreasing the sensitivity of the catalyst to substances which diminish its activity. Thus admixture of copper with nickel in the hydrogenation of oils appears to increase the ruggedness of the catalytic agent and to render it less sensitive to traces of such negative catalysts as carbon monoxide."

There seem to be at least four possible hypotheses in regard to the effect which a change in the structure of a catalytic agent has on the apparent reaction temperature.

1. The effect may be chiefly a question of total surface. Increasing the surface increases the adsorption per unit mass of the catalytic agent but not necessarily the adsorption per unit surface. With increasing surface there will be more reaction per unit mass in unit time, and consequently a reaction might be detected at a lower temperature than would otherwise be the case. It does not seem very probable that the increase in surface on activation is enough to account for the observed lowering of the apparent reaction temperature; but this is a question for quantitative measurements.

2. With increased surface and consequently reaction per unit mass of catalytic agent there will be increased evolution of heat per unit time. Unless suitable cooling is supplied, the temperature

will rise. Since a porous catalytic agent is not a first-class conductor of heat and since the contact reactions are mostly exothermal, it is certain that the temperature at the contact surface is higher than the apparent temperature of the catalytic agent. It is a matter of quantitative measurements to determine whether the lowering of the apparent reaction temperature is real or illusory.

3. Changing the form of the surface may change the surface in such a way that the adsorption per unit surface is increased. This may very well be. While Langmuir claims that the adsorption layer is only one or two molecules thick on a plane surface, he is willing to admit that this may not hold true for a porous mass.

4. The change in the surface may be such that the reaction products pass off more rapidly and therefore do not slow down the reaction. If there were pockets, for instance, in the catalytic agent, the reaction products would be removed only by diffusion. With an open structure, they would be swept out by the incoming gas stream and this might easily have a very marked effect on the reaction velocity.

We are not in a position to tell to what extent any or all of these four hypotheses will account for the facts. It may be that other supplementary hypotheses are necessary. We do not know whether the physical disintegration of the catalytic agent is due to the formation and decomposition of definite or indefinite chemical compounds or whether it is chiefly the result of a heat effect.

It seems to me that the study of organic reactions is by far the most likely to prove fruitful. The reactions can take place in more different ways than with inorganic reactions and the intermediate compounds are easier to isolate and identify. The apparent theoretical simplicity of the catalysis of oxyhydrogen gas or of the synthesis of ammonia is deceptive. We know the initial and final states only. The problem of contact catalysis is not a problem for the physical chemist alone. It is a problem to be worked out jointly by the physical chemist and the organic chemist.

In at least two instances it should be relatively simple to determine the reacting radicals. If we pass a mixture of ethyl acetate and hydrogen over pulverulent nickel, it is probable that some or all of the initial products will be reduced before they have time

to react in the normal way. A study of the reaction products will therefore throw light on the probable mechanism of the reaction which occurs in the absence of hydrogen. If we obtained CH_4 and $HCO_2C_2H_5$, for instance, we should conclude that the original break had been into CH_3 and $CO_2C_2H_5$. If we found CH_3CO_2H and C_2H_6, we should conclude that these were reduction products of CH_3CO_2 and C_2H_5. If the reaction products were CH_4, C_2H_6 and CO_2 or some reduction product of this last, we should undoubtedly assume that ethyl acetate splits simultaneously into CH_3, CO_2 and C_2H_5.

If ether is passed over pulverulent nickel, the dissociation will probably be to $C_2H_5O + C_2H_5$ or to $C_2H_5O\ C_2H_4 + H$. In the first case the final products will be $2C_2H_4$ and H_2O just as with alumina. In the second case they are likely to be $CH_3CHO + C_2H_4 + H_2$, though the ethylene and hydrogen may combine more or less completely to form ethane.

These two illustrations are sufficient to indicate the kind of work that I believe ought to be done and the organic chemists will undoubtedly be able to develop this suggestion in most unexpected ways.

This outline of the present status of the problem of contact catalysis enables us to formulate a number of problems which ought to be carried out in order to clear up the general subject, after which, or along with which, a study should be made of the actual processes involving contact catalysis, so as to be able to classify them. The following list of general problems is suggested tentatively:

1. Study of action, if any, of infra-red radiation on methyl acetate solution.

2. Study of radiation effects, if any, of any of the contact catalysts.

3. Adsorption of reacting substances and reaction products.

4. Adsorption of mixed gases.

5. Adsorption of poisons.

6. Adsorption of reacting substances and reaction products by poisoned catalytic agent.

7. Rates of adsorption of reacting substances and reaction products by poisoned catalysts.

8. Effects of structure of catalytic agent.

9. Effects of traces of other substances on catalytic agents.

10. Study of action of promoters, including adsorption.

11. Identification of intermediate compounds involving the catalyst.

12. Intermediate stages in organic decompositions.

13. Determination of reversible equilibria in cases of contact catalysis.

14. Study of false equilibria.

15. Study of over-voltage as a problem in contact catalysis.

16. Determination of all possible catalytic reactions with all possible porous substances.

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COLLOID CHEMISTRY AND ELECTROCHEMISTRY[1]

By Wilder D Bancroft.[2]

ABSTRACT.

A resumé of phenomena which are both colloidal and electrochemical, or cases where one results from the other, such as precipitation of colloids by electrolytes, formation of colloidal solutions by arcs or by electrochemical action or by spraying liquid metal and fusion. Migration of colloidal particles under electrochemical potential, cataphoresis and electrical endosmose, the functioning of a diaphragm, are discussed; also the effect of colloids on the conductivity of solutions, the action of electrolytes on living tissues, electrostatic precipitation of extremely small particles, electrification of the air and of suspended dust clouds, and metallic fogs or mists in fused electrolytes. [J. W. R.]

It has seemed worth while to discuss a few of the points at which colloid chemistry and electrochemistry come in contact. A solid shows selective adsorption from solution and consequently may adsorb certain ions preferentially. In general a solid salt has a marked adsorbing power for its own ions. Thus silver bromide adsorbs silver and bromine ions strongly, potassium and nitrate ions but slightly. Beyond this we cannot go with any definiteness, though it is often true that hydrogen and hydroxyl ions are adsorbed more strongly than the other ions and that ions of higher valence are often adsorbed more strongly than those of lower valence (Schulze's law). Osaka[3] found that potassium salts are adsorbed more strongly by charcoal than the corresponding sodium salts. The percentage adsorptions for normal solu-

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[3] Mem. Coll. Sci. Kyoto Univ. (1915), 1, 257.

tions of KI, KNO_3, KBr, KCl and K_2SO_4 are approximately 28, 16, 14, 7 and 5 respectively, showing that the order of adsorption of the anions is $I > NO_3 > Br > Cl > SO_4$. Rona and Michaelis[4] find that the order of adsorption of the anions is $OH > CNS > I > NO_3 > Br > Cl > HPO_4 > SO_4$, and of the cations is $H > Al > Cu > Zn > Mg > Ca > NH_4 > K > Na$. Weiser and Sherrick[5] find that the order of adsorption of anions by barium sulphate is ferrocyanide > nitrate > nitrite > chlorate >permanganate > ferricyanide > $Cl > Br > CN > CNS > I$, the relative adsorption of chlorine, bromine, and iodine ions being just the reverse with barium sulphate from what it is with charcoal.

Selective adsorption connotes the possibility of chemical decomposition as a result of adsorption. If a given substance adsorbs a base more strongly than an acid, for instance, there will be a tendency for the salt of that base and that acid to hydrolyze, the base being then adsorbed more strongly than the acid. The weaker the acid, the less will be its solvent action and consequently the greater the hydrolysis.[6]

Charcoal adsorbs aniline less strongly than benzoic acid and more strongly than acetic acid.[7] Consequently, if solutions of aniline benzoate and aniline acetate are shaken with charcoal, the first becomes less acid and the second more acid. Still more interesting is the behavior of aluminum and chromic salts with gelatine where the salts are split into free base and free acid, both being adsorbed simultaneously but separately.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptize the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion. Freshly precipitated silver halides are peptized by dilute silver nitrate or by the corresponding potassium halide.[8] Many oxides are peptized by their chlorides or nitrates, forming so-called basic salts.[9] Sulphides are peptized by hydrogen sulphide.[10] Gelatine is lique-

[4] Biochem. Zeit. (1919), 94, 240.
[5] Jour. Phys. Chem. (1919), 23, 205.
[6] Cf. Liebermann: Sitzungsber. Akad. Wiss. Wien (1876), 74, 331.
[7] Freundlich and Masius: Van Bemmelen Gedenkboek (1910), 100.
[8] Lottermoser: Zeit. phys. Chem. (1908), 62, 371.
[9] Graham: Jour. Chem. Soc. (1862), 15, 254; Müller: Zeit. anorg. Chem. (1907), 52, 316; Szilard: Jour. chim. phys. (1907), 5, 488, 636.
[10] Young: Jour. Phys. Chem. (1917), 21, 1, 14.

fied or peptized by a potassium iodide solution.[11] The peptization of hydrous oxides by caustic alkali can be considered as a case of a common ion or as the preferential adsorption of hydroxyl ion. Hydrous chromic oxide gives an apparently clear, green solution when treated with an excess of caustic potash; but the green oxide can be filtered out completely by means of a collodion filter, a colorless solution passing through.[12]

A colloidal solution is stable when the particles are sufficiently small to be kept up by the Brownian movements and when they are prevented in some way from coalescing. One way of preventing agglomeration is by means of adsorbed ions. So long as the particles are all charged positively or all charged negatively, they will tend to repel one another and will not coalesce unless the concentration is too high. If the electrical charge is neutralized or counterbalanced in any way, the particles which have been stabilized by an adsorbed ion will agglomerate[13] unless some other factor comes into play. Such colloidal solutions will be very sensitive to electrolytes having a readily adsorbable ion of the opposite charge from that which stabilizes the particles. These solutions precipitate completely at the iso-electric point, as it is called, where the electrical charge is neutralized or counterbalanced.

If the particles of a given colloidal solution are charged positively by adsorbed hydrogen ions, for instance, they will be precipitated by the addition of an electrolyte with a readily adsorbed anion. Since this is a matter of selective adsorption, the concentration at which an electrolyte will precipitate a colloidal solution will depend on the nature of the cation, the anion, and the dispersed phase. The order of concentrations at which electrolytes precipitate a given colloidal solution is a measure of the order of adsorption of the ions in question. The order thus obtained is not necessarily the same as the order in which the salts, when present in excess, are adsorbed by the solid. Precipitated charcoal, for instance, adsorbs ions and salts, and this adsorption may vary considerably from that necessary to precipitate charcoal from suspension. Weiser and Middleton[14] find that the order of

[11] Briggs and Hieber: Jour. Phys. Chem. (1920), **24**, 74.
[12] Nagel: Jour. Phys. Chem. (1915), **19**, 331, 569.
[13] Hardy: Zeit. phys. Chem. (1900), **33**, 285; Burton: Phil. Mag. (1906) [6], **12**, 472; (1909), **17**, 583.
[14] Jour. Phys. Chem. (1920), **24**, 30.

precipitation of colloidal ferric oxide by anions is bichromate > tartrate > sulphate > citrate > oxalate > iodate > phosphate, while the order of adsorption of the salts when ferric oxide is precipitated in presence of a definite excess of salt is phosphate > citrate > tartrate > oxalate > iodate > bichromate. In addition to the extra adsorption in presence of an excess of salt, there is also the adsorption of the undissociated salt which may and apparently does change things very much.

An interesting case of the precipitation of a colloid by an electrolyte is to be found in the action of sea-water on muddy river water. Skey[15] pointed out that suspended mud is precipitated by electrolytes, and Waldie[16] has discussed the clearing of the water of the Hooghly. When a river flows into the ocean, the current becomes less and some of the suspended mud is dropped on this account; but that is relatively unimportant in many cases. Schloesing[17] called attention to the fact that the formation of deltas is due primarily to the coagulation of the suspension by the electrolytes in the salt water.

If we mix colloidal solutions of two substances, each of which adsorbs the other, the mutual adsorption will have some effect on the adsorption of the peptizing agent. If it causes a decrease in the adsorption of the peptizing agent, this means a decreasing stability of the colloidal solution and may lead to precipitation over some range of relative concentrations. In case this occurs, we shall have colloidal solutions of decreased stability when either colloid predominates sufficiently and precipitation for intermediate relative concentrations. The range over which precipitation occurs may be great or small, depending on the ease with which the peptizing agent is displaced or neutralized.

The most familiar case of such precipitation is when we are dealing with two colloids having opposite electrical charges. This point was studied carefully by Biltz[18] and the general statement is to be found in all the text-books on colloid chemistry. The negatively charged colloids studied by Biltz were platinum, gold, selenium, cadmium sulphide, antimony sulphide, arsenic sulphide, stannic oxide, molybdenum blue (Mo_3O_8), tungsten blue (W_2O_3), and vanadium pentoxide. The positive colloids were

[15] Chem. News (1868), 17, 160.
[16] *Ibid.* (1874), 30, 37.
[17] Jour. Chem. Soc. (1871), 24, 750.
[18] Ber. deutsch. chem. Ges. (1904), 37, 1095.

the oxides of iron, aluminum, chromium, thorium, zirconium, and cerium. Precipitation occurs when each positive colloid is mixed with each negative colloid in proper proportions. Biltz was interested in determining the concentrations at which the most complete precipitation takes place; but he was not especially interested in the rather vague points at which precipitation does not take place. While his data are quite sufficient to show that precipitation is specific,[19] they are hardly adequate to show that the range varies markedly with different substances.

Since a colloid peptized by water may be charged positively or negatively, there is no reason why it should not precipitate another colloid under suitable conditions. We usually consider the colloids peptized by water solely as protecting colloids, but this is clearly an inadequate view, as is shown by the experimental data. Years ago Schulze[20] pointed out that small amounts of a gelatine solution were as effective as lime or alum in causing the rapid sedimentation of clay and that addition of minute quantities of gelatine to barium sulphate simplified the question of filtration and washing very much. He, of course, gave no adequate explanation of the phenomenon, and the real explanation was given by Billitzer,[21] who called attention to the fact that while galatine, agar-agar, etc., ordinarily check the precipitation of colloidal solutions by electrolytes, small amounts of these same substances may have a precipitating action. This can be detected even when the gelatine produces no precipitation itself.

Billitzer cites the experiments of Neisser and Friedemann, in which it was found that a mastic emulsion containing a trace of gelatine was precipitated more readily by sodium than when no gelatine is present. Billitzer finds that gelatine precipitates such negative colloids as antimony sulphide and arsenic sulphide in acid or neutral solution, but does not precipitate positively charged sols such as hydrous ferric oxide. Gelatine in ammoniacal solution precipitates hydrous ferric oxide, though no precipitation occurs if ammonia is added to a mixture of gelatine and ferric oxide. Bismarck brown, which is a positive colloid, is precipitated by an alkaline gelatine solution, while eosine is precipitated by an acidified gelatine solution.

[19] Bancroft: Jour. Phys. Chem. (1915), 19, 363.
[20] Pogg. Ann. (1866), 120, 369.
[21] Zeit. phys. Chem. (1905), 51, 145.

If the ratio of gelatine to the other colloid is increased sufficiently, we shall pass through the precipitation range into the range where the colloidal solution is stabilized by gelatine and then behaves more like a water-soluble colloid. Colloidal gold and colloidal silver solutions, when stabilized by gelatine, can be evaporated and re-dissolved because the gelatine prevents the irreversible agglomeration. When less gelatine is used it may retard, though not prevent, the change of red colloidal gold to blue.

Biltz[22] obtained no precipitation upon mixing any two of his positively charged sols and no precipitation on mixing any two of the negatively charged sols except when gold or selenium was mixed with the sulphides and there chemical action probably took place. Biltz concluded that sols of like charge had no effect upon each other; but this does not follow, because adsorption of one colloid by the other would not neutralize the electrical charges and therefore would not cause precipitation. In certain cases we know that there is adsorption. In alkaline solutions peptized chromic oxide holds up ferric oxide if the latter is not present in too large amounts[23] and is carried down completely by it if the ferric oxide is present in excess. Other cases of the same type could be cited. The fact that gelatine protects ferric oxide when added before the ammonia shows that it must have been adsorbed by the ferric oxide. Bechhold[24] has shown that an ultra-filter which will stop Prussian blue and will let arsenic sulphide pass, holds back the arsenic sulphide when mixed with Prussian blue. Although both are negatively charged sols, it seems evident that there is a mutual adsorption. On the other hand, Bechhold found that hemoglobin can be separated from Prussian blue by filtration through a suitable ultra-filter, the hemoglobin going through the filter. In this case there is no appreciable adsorption.

Two methods of forming colloidal solutions electrically are of interest to us. When a direct current arc is formed under water between two wires, the metal is disintegrated and colloidal solutions of platinum, iridium, palladium, gold, silver, and cadmium may be obtained in this way.[25] Satisfactory conditions are obtained with 30 to 40 volts and 5 to 10 amperes. A trace of alkali

[22] Ber. deutsch. chem. Ges. (1904), 37, 1095.
[23] Northcote and Church: Jour. Chem. Soc. (1854), 6, 54; Nagel: Jour. Phys. Chem. (1915), 19, 331.
[24] Zeit. phys. Chem. (1907), 60, 299.
[25] Bredig: Zeit. Elektrochemie (1898), 4, 514; Zeit. phys. Chem. (1899), 31, 258.

in the water causes formation of finer particles, presumably owing to the stabilizing of the hydroxyl ion. The disintegration is chiefly at the cathode.

The method is not satisfactory with organic liquids, because too much decomposition of the liquids takes place. Svedberg found empirically that this decomposition could be decreased very much if the current density were made as small as possible.[26] He therefore used an oscillatory discharge from an induction coil with a condenser in parallel or in series. The best results are obtained with large capacity, small self-induction, low resistance, and short arc.[27] By this improved method Svedberg succeeded in preparing colloidal solutions of all the metals, including the alkali metals. Liquid methane, ether, and isobutyl alcohol at low temperature were especially satisfactory with the metals of the alkalies and the alkaline earths. The order of disintegration of some of the metals under similar conditions was found to be Fe, Cu, Ag, Al, Ca, Pt, Au, Zn, Sn, Cd, Sb, Tl, Bi, Pb, the iron being the least rapidly disintegrated and the lead the most rapidly. There is no apparent relation either with the order of the boiling-points or with the order of disintegration by cathode rays or canal rays.

Schoop[28] has developed a process for plating metals on all sorts of materials by blowing compressed air at about five atmospheres pressure through a pointed nozzle into an arc playing between two wire terminals. Smooth, well-adhering deposits of sprayed metal are obtained when aluminum or copper is sprayed on glass in this way, and the metal adheres so tenaciously that it is impossible to remove the film without destroying the glass surface. It is claimed that a microscopic examination showed that the surface of the glass melts and that the metal is practically fused into the glass. This will happen only when the object to be coated is placed very close to the arc. By working at a longer range it is possible to coat combustible materials like paper and celluloid. It is possible to obtain deposits of brass by making one pole of copper and the other of zinc.

[26] Svedberg: Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe (1909), 424.

[27] See also Morris-Airey and Long: Jour. Chem. Soc. (1913), **104**, II, 1033; Long: Zeit. Kolloidchemie (1914), **14**, 136; Kutscheroff: *Ibid.* (1912), **11**, 165; Sawrieff: Zeit. phys. Chem. (1914), **87**, 506.

[28] Chem. Abs. (1919), **13**, 2640.

With a lead cathode in caustic soda solution, the lead disintegrates when the current density exceeds a critical value, and the solution is colored black like ink with fine particles of metallic lead.[29] This is due to the temporary formation of a sodium-lead alloy, which then disintegrates in contact with water. Similar results can be obtained with cathodes of tin, bismuth, thallium, arsenic, antimony, and mercury. E. Müller[30] obtained colloidal solutions of tellurium with a tellurium cathode. This seems to be due to the formation of polytellurides, which break down and set free tellurium. In the presence of oxygen there may be also an oxidation of a telluride. Fischer[31] has obtained metallic copper in the solution by using a high current density with a copper anode in sulphuric acid. Cuprous sulphate is formed, which breaks down to metallic copper and cupric sulphate. This experiment has not yet been made to give colloidal copper; but this could probably be done if one were to add a suitable protecting colloid. The disintegration of all electrodes by an alternating current when the current density is high is undoubtedly due to the temporary formation and subsequent breaking down of a hydrogen or metallic alloy.[32]

If a particle suspended in a liquid adsorbs a free ion, the charged particle will then behave to some extent like an ion and will tend to move under electrical stress toward the cathode if the adsorbed ion is positive and toward the anode if the adsorbed ion is negative.[33] Reference has been made to the fact that silver bromide particles move to the cathode when stabilized by silver ions and to the anode when stabilized by bromine ions. By following the electrolysis under the microscope it is possible to determine the rate of movement of a suspended particle for a given difference of electrical potential. The rate of migration of colloidal particles is of the same order as that of ions.[34] Thus colloidal silver moves with a velocity of 2.0-3.8 μ/sec. under a potential drop of one volt per centimeter, and colloidal gold at about 4.0 μ/sec., while the chlorine ion gives a value of 6.8 μ/sec.

[29] Reed: Jour. Franklin Inst. (1895), 139, 283; Bredig and Haber: Ber. deutsch. chem Ges. (1898), 31, 2741; Haber and Sack: Zeit. Elektrochemie (1902), 8, 243; Zeit. anorg. Chem. (1903), 34, 286.

[30] Zeit. Elektrochemie (1905), 11, 521, 701; Haber: *Ibid.* (1905), 11, 660, 827.

[31] *Ibid.* (1903), 9, 507.

[32] Haber: Trans. Am. Electrochem. Soc. (1902), 2, 192; Van Name: Zeit. Elektrochemie (1904), 10, 303.

[33] Linder and Picton: Jour. Chem. Soc. (1897), 71, 568.

[34] Zsigmondy: The Chemistry of Colloids (1917), 46.

Billitzer [35] has attempted to determine absolute potential differences by finding solutions in which a given colloidal metal did not move under electrical stress. While the method is good in principle, one cannot reason from the adsorption of a finely divided metal to the adsorption of massive metal. It seems possible that definite results might be obtained if the problem were attacked with a better knowledge of colloid chemistry. Since the colloidal particle moves in one direction with reference to the water, the water moves in the opposite direction relatively to the particle. This can be shown if we keep the colloidal particles stationary in the form of a diaphragm.

The electrical transfer of particles through the liquid is called cataphoresis and the transfer of liquid through a stationary diaphragm is called electrical endosmose. It was first observed by Reuss at Moscow in 1808. Working with so-called pure water it is found that water passes to the cathode when the porous diaphragm is made of glass, shellac, earthenware, carborundum, asbestos, wool, cotton, platinum, silver, arsenic, sulphide, or sulphur; and to the anode when the diaphragm is chromic chloride, cobalt oxide, zinc oxide, or barium carbonate.[36] When turpentine was substituted for water, it moved to the anode with all diaphragms except sulphur. Coehn[37] has attempted to account for this by postulating empirically that when two non-miscible substances are in contact, one being a pure liquid, the substance with the higher di-electric constant is charged positively with reference to the one with the lower di-electric constant. This rule applies in the case of water and turpentine where the di-electric constants are 81 and 5 respectively, but it is by no means absolute even for pure liquids,[38] and breaks down completely when applied to aqueous solutions. The phenomenon depends on the relative adsorption of ions, and Coehn's rule is a useful first approximation in certain cases.

Since the charge on the diaphragm depends on the nature of the ion adsorbed, it follows that an aqueous solution may flow one way or the other through a given diaphragm, depending on the nature of the dissolved substance. This was brought out

[35] Drude's Ann. (1903), 11, 902, 927.
[36] Quincke: Pogg. Ann. (1859), 107, 1; (1860), 110, 38. Actually Quincke forced water through the diaphragms and noticed the change.
[37] Wied. Ann. (1898), 64, 227; Zeit. Elektrochemie (1910), 16, 586.
[38] Briggs: Jour. Phys. Chem. (1917), 21. 204.

clearly by Parker,[39] and was emphasized by Perrin,[40] who found a reversal in many cases when the solutions were alkaline instead of acid. Every diaphragm tends to become charged positively in an acid solution and negatively in an alkaline solution. Every ion of unlike sign tends to neutralize the charge on the diaphragm. Perrin believed that the effect of other ions was more marked the greater the valence; but this is true only in so far as the ion with the higher valence is adsorbed more strongly than the ion with a lower valence[41]; in other words, in so far as Schulze's so-called law holds. In some cases the agreement is very good. Thus in acid solutions the flow through the diaphragm to the anode increases as the anion changes from quadrivalent ferrocyanide to bivalent sulphate to univalent chloride, because the adsorption of the anion decreases in the same order and the diaphragm becomes charged more positively.

In alkaline solution the flow to the cathode increases as the cation changes from trivalent lanthanum to bivalent barium to univalent sodium. On the other hand, with a porous cup in a slightly acidified copper sulphate solution the flow is to the cathode, apparently because copper ions are not adsorbed to any great extent, while the adsorption of sulphate ions exceeds the adsorption of hydrogen ions because the concentration of the first is so much greater than that of the second. With a slightly acidified copper nitrate solution the flow is to the anode, because the nitrate ions are not adsorbed very much and the hydrogen ions determine the direction of the flow.

Much to Perrin's surprise a barium carbonate solution acted in one case as though it were an acid. This is undoubtedly because of the preferential adsorption of barium ions which charge the diaphragm positively.

In electrolytic reductions of organic substances in aqueous alcoholic solutions using a porous cup, the flow of liquid to the cathode may be quite annoying. Owing to the lower di-electric constant of alcohol, the normal tendency of the liquid to go to the cathode becomes less, but the increased resistance would increase the flow and nothing is known in regard to adsorption from

[39] Johns Hopkins Dissertations (1901), **31**, 23; Briggs: Jour. Phys. Chem. (1917), **21**, 235.

[40] Jour. Chim. phys. (1904), **2**, 601.

[41] Elissafoff: Zeit. phys. Chem. (1912), **79**, 285.

these solutions. Billitzer[42] found that colloidal platinum is charged positively in aqueous alcohol though negatively in pure water.

The amount of liquid transferred by electrical endosmose increases with rising temperature, the increase being nearly proportional to the change in the fluidity[43] (the reciprocal of the viscosity).

The commercial applications of electrical endosmose have not been very successful. Count Botho Schwerin[44] took out a number of patents for removing water from peat. Starting with a peat mud containing about 90 percent moisture, he claimed that the moisture content could be reduced to 65 percent at an expenditure of about 15 KW.H. per cubic meter of water removed, the best potential gradient being 4-5 volts per centimeter. The cost of drying from 65 percent moisture to 20 percent moisture was so great that the process was not a success. It is reported that electrical endosmose has been used successfully in the dye industry in the drying of pastes. Electrical tanning has also been tried, the tanning liquor being carried into the hides by electrical endosmose. This seems to have failed in part on account of the oxidation of the tannin at the anode. Cataphoresis is made use of in electrolytic refining and plating, the use of addition agents being essential in some cases.[45]

There are no very definite results as to the effect of colloids on the conductance of solutions,[46] but it is evident that an adsorbed ion cannot have as high a migration velocity as an unadsorbed ion, and that consequently the presence of a colloid must decrease the conductance to some extent, depending on the amount and nature of the ions adsorbed. If a clay suspension is stirred,[47] the conductance may increase because the adsorbed ions which are carried down when the suspension settles are brought up between the electrodes. McBain[48] found that certain solutions of sodium palmitate conducted well, although the freezing points of the solutions were only enough to account for the sodium ions. It is probable that we have hydrolysis to caustic soda and col-

[42] Zeit. phys. Chem. (1903), **43**, 312.
[43] Briggs, Bennett and Pierson: Jour. Phys. Chem. (1918), **22**, 256.
[44] Zeit. Elektrochemie (1903), **9**, 739.
[45] Müller and Bahntje: Zeit. Elektrochemie (1906), **12**, 317.
[46] Wo. Ostwald: Van Bemmelen Gedenkboek (1910), 367.
[47] Bleininger: Am. Ceramic Soc. (1913), **15**, 343.
[48] Jour. Chem. Soc. (1914), **105**, 965.

loidal palmitic acid, the latter[49] then adsorbing hydroxyl ions, just as we know that silicic acid adsorbs hydroxyl ions and is peptized by them.

This suggests an interesting theoretical possibility. Suppose we have two sets of finely divided particles neither of which adsorbs the other appreciably, and let us also suppose that one set of particles adsorbs a given cation very strongly while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well but which will contain no free ions to speak of because, by definition, the cations have been practically completely adsorbed by one set of particles and the anions by the other set of particles. It is not known whether these limiting conditions can all be fulfilled simultaneously. A possible case would be the mixing of dilute solutions of silver sulphate and lead chloride. The lead sulphate would adsorb sulphate or lead ions strongly and the silver chloride would adsorb chloride or silver ions strongly. Nobody knows what each would do to the other.

While an adsorbed ion may increase the conductance of a liquid, it will behave quite abnormally as regards electrometric measurements. An adsorbed chlorine ion will not give a test with silver nitrate and consequently will have only a negligible effect on a chlorine electrode. It is not probable that an adsorbed hydrogen or hydroxyl ion behaves electrochemically like a free hydrogen or hydroxyl ion. This possible error has been overlooked in many cases where the hydrogen electrode has been used. Another source of error in electrometric measurements with colloidal solutions is to neglect the fact that we are not dealing with true solutions. If we measure a copper electrode in a solution of alkaline copper tartrate we find that the concentration of copper ions is extremely low. That is all that the measurement tells us. If the copper is in true solution, it must be present as a complex salt, as is unquestionably the case with potassium silver cyanide. If we have peptized copper oxide or hydroxide present, there is no need to assume the existence of a complex copper salt at all.

The true interpretation of the phenomena cannot be made until

[49] There may also be adsorption by colloidal sodium palmitate.

we know whether a so-called alkaline copper tartrate solution is a true solution or not. We cannot answer this question at present. On the other hand, it seems practically certain that the effect of sugars in preventing the precipitation of the heavy metal hydroxides by alkalies is due to the formation of colloidal solutions. Consequently the conclusions drawn from electrometric measurement of such solutions are necessarily false. We know that indicators may give hopelessly wrong information as to hydrogen ion concentration when used in presence of colloids.

The study of colloid chemistry has helped enormously to throw light on some of the phenomena of the action of electrolytes on living tissues. Loeb has shown that there are certain organisms which flourish in salt water and which die in fresh water. That could be accounted for on the assumption that the difference in osmotic pressure inside and outside of the organism caused them to swell up and burst when placed in fresh water. Unfortunately, when these organisms were placed in sodium chloride solution or in calcium chloride solution isotonic with the sea-water, they died about as promptly as in fresh water. The important thing was a ratio of calcium to sodium and that could not be accounted for on the basis of osmotic pressure. Also Osterhout has shown that the specific conductance of certain tissues were decreased by addition of calcium salts and increased by addition of sodium salts.

We know that sodium soaps tend to emulsify oils in water while calcium soaps tend to emulsify water in oils. If now we consider protoplasms as analogous in some way to an emulsion with the lipoid material functioning as the oil, we see that some definite ratio of calcium to sodium will keep the protoplasm just on the border line between oil in water and water in oil.[50] If this is the condition necessary for life, it is easy to see why the marine organisms could not flourish either in a pure sodium chloride solution or in a pure calcium chloride solution, no matter what the concentration might be. Since an emulsion of water in oil will conduct less well than an emulsion of oil in water, it is easy to see why addition of calcium salts decreased the specific conductance and addition of sodium salts increased it. By precipitating an emulsion in the pores of a very fine-grained filter

[50] Clowes: Jour. Phys. Chem. (1916), 20, 407.

paper, Clowes[51] was able to duplicate Osterhout's results very closely.

The work of Cottrell[52] on the electrical precipitation of solid and liquid particles is so familiar that I need only refer to it. It is a brilliant application of electrochemistry to a problem in colloid chemistry. A modification of the apparatus has recently been made for the study of toxic smokes in the laboratory.[53] The apparatus consisted essentially of a central wire cathode surrounded by a cylindrical anode of aluminum foil 0.001 inch in thickness. An alternating current running up to 15,000 volts was rectified by means of a General Electric Company "Kenotron." Complete precipitation could be obtained even when smoke was drawn through the apparatus at a rate of about five liters per minute. The anode could be removed and weighed, thus giving a satisfactory method of determining the concentration of any smoke. Examination of the precipitate microscopically makes it possible to tell whether one is really dealing with a smoke or with a fog.

When dust is blown about by the wind, it becomes electrified.[54] In South Africa, at Bloemfontein, at an elevation of 4,500 feet, the normal fine weather charge of the air is positive and seldom exceeds a maximum value of 200 volts per meter. During a dust storm the sign of the charge changes and the value may exceed 500 volts per meter. A so-called dust devil or whirlwind which carries a column of fine sand up two or three hundred feet in the air will affect an instrument two miles away, reversing the charge. This is because the sand particles are charged positively. In England a cloud of dust increases the positive charge in the air instead of decreasing it. This is because the dust in England is usually calcareous and acquires a negative charge. It is also known that red lead acquires a positive charge when blown into the air and sulphur a negative one.

From the experiments that he made, Rudge deduced four generalizations.[55] Non-metallic elements give positively charged clouds when the finely-divided solid material is blown into a cloud by a current of air. Metallic elements give negatively charged

[51] Clowes: *Ibid.*
[52] Jour. Ind. Eng. Chem. (1911), 3, 542.
[53] Tolman, Reyerson, Brooks and Smyth: Jour. Am. Chem. Soc. (1919), 41, 587.
[54] Rudge: Phil. Mag. (1912) (6), 23, 852; (1913), 25, 481.
[55] Cf. Knoblauch: Zeit. phys. Chem. (1902), 39, 225.

clouds when the finely-divided material is blown into a cloud by a current of air. Solid acid-forming oxides give positively charged clouds, and basic oxides negatively charged clouds. In the case of salts the charge apparently depends on the relative strength of adsorption of positive and negative ions. The whole subject of frictional electricity should be gone over from the viewpoint of adsorption of ions. If this were done, it would undoubtedly bring some order out of the present chaos.

Dewar[56] states that if a glass rod is cooled to the temperature of liquid air and is then brought into the air of the room, moisture will condense on it as a sheet of ice. If the glass rod is electrified by contact with a piece of silk, the ice forms as a forest of crystals and not as a sheet. The reason for this seems to be that the ice particles are themselves electrified and consequently precipitate as far from each other as possible. This observation may have a bearing on some of the sedimentation problems.

Platinum mirrors were obtained by Wright[57] by electrical disintegration of platinum wires, and by Edison[58] by volatilization of electrically heated platinum in hydrogen. Cottrell[59] modified the method of electrical disintegration so as to obtain platinum black.

The adsorption of a solid by a solid is very important in the case of aluminum and nickel because the adsorbed oxide films are the reason why these metals resist corrosion as well as they do. If iron formed a similar, coherent film, the problem of rusting would not be a serious one. Passive iron owes its peculiar properties to the adsorption and stabilization of a higher oxide,[60] either FeO_2 or FeO_3. It is probable that vermilion is adsorbed by copper because De la Rue[61] says that electroplated copper blocks cause vermilion to blacken, while cast copper does not.

Lorenz[62] has shown that the fused baths, from which we obtain sodium, aluminum, and other metals electrolytically, tend to peptize the molten metal. The amount of peptization or production of metallic fog increases very rapidly with rising temperature,

[56] Chem. News (1908), 97, 5.
[57] Am. Jour. Sci. (1877) [3], 14, 169.
[58] Chem. News (1879), 40, 152.
[59] Zeit. phys. Chem. (1903), 42, 385.
[60] Bennett and Barnham: Jour. Phys. Chem. (1917), 21, 107.
[61] Mem. Chem. Soc. (1845), 2, 305.
[62] Van Bemmelen Gedenkboek (1910), 395.

which is one reason why it is very important to carry on the electrolysis at as low a temperature as possible.

There has been so much discussion of the importance of addition agents in electroplating that a reference to this branch of colloid chemistry is sufficient. Since I have nothing at present to add to what I said at the Pittsburgh meeting in regard to overvoltage and to its application to electrolytic reductions and oxidations, I refer to that paper.[63]

The problem of the electrical resistance of alloys is similar to some extent to the one in regard to the conductance of emulsions. If one of the phases of a binary alloy conducts much better than the other, it will make a great difference whether the better conducting phase is the external or the internal phase. An intermediate case occurs when the two phases are each continuous, forming what I have called an interlacing system.

The properties of graphite and carbon electrodes depend in part on their structure. If we could make a fused graphite or carbon electrode, for instance, its properties would be quite different from those of the electrodes we now have. We do not know whether Chaney's "gas-treated" carbon is another modification or whether it is perhaps graphite adsorbed by carbon.

Cornell University.

DISCUSSION.

MR. WILSON: Would you mind reproducing that gelatine diagram there?

(President Bancroft drew the diagram on the blackboard.)

MR. WILSON: Your scales for barium sulphate and gelatine are entirely different, are they not?

W. D. BANCROFT: Oh yes. I was not bothering about the quantitative side of it. We haven't any data for doing it quantitatively at all, but I was merely considering the thing from left to right.

[63] Bancroft: Trans. Am. Electrochem. Soc. (1917), 32, 439.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

"SETTLING" PROBLEMS.[1]

By WILLARD A. DEANE.[2]

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SETTLING PROBLEMS.

Settling problems are of such common occurrence that we are all more or less familiar with their general nature. Primarily they are concerned with the settling of solid particles in a suspension, to permit a separation and removal of two products, namely a supernatant liquid and a settled sludge, meeting certain required conditions as to degree of clarity and density respectively. Although every settling problem involves the calculation of a tank of proper dimensions to furnish these conditions, its ultimate solution requires that the tank size be within commercial limits, and a careful study of a great number of factors must be made before any conclusion can be reached. The wide difference not only in the various materials encountered and the physical character of the medium in which they are suspended, but also in the imposed conditions, both from a physical and commercial point of view, have a most important bearing in effecting a proper solution. To accomplish these results, a thorough understanding of the physics of settling and the agencies governing its control is essential.

In practice, settling methods are divided into the following two general types:

1. Intermittent.
2. Continuous.

1. Intermittent Settling.

The intermittent type is the simplest and oldest method for carrying on sedimentation. The apparatus used, commonly known as a "Settling Box," is nothing more than a tank of any convenient shape, often rectangular, with means for removing clarified liquid and the settled sludge.

The operation consists in filling the "settling box" with the suspension or pulp under treatment, allowing the solids to settle undisturbed for a period of time sufficient to effect the desired degree of clarification, and then removing the top liquor, either by syphoning or by decanting and discharging the sludge through an outlet pipe at the bottom. This is necessarily an intermittent operation and occurs in cycles in which charging, settling and discharging follow in consecutive order.

2. Continuous Settling.

In continuous settling a continuous feed is supplied to a tank that permits a continuous overflow of liquid clarified to the required degree and a continuous discharge of solids with lowest permissible moisture content. Although continuous methods have been applied to the ordinary "settling box" the results are far from satisfactory owing to the fact that the thickened sludge builds up and is impossible of removal in continuous and regulated amounts.

As a consequence continuous settling had little application until the introduction of the Dorr Continuous Thickener which demonstrated the practicability and advantages of continuous settling over intermittent settling, and has resulted in a greatly increased application of settling methods.

Continuous Thickener: The continuous thickener embodies two essential components, the tank proper and the mechanism. The mechanism is the vital feature, for it is by reason of this development that a continuous and even discharge of thickened sludge is made possible. Briefly, it consists of a slowly revolving vertical shaft, at the bottom of which are attached four radial arms with plows so arranged that their circular movement over the bottom of the tank draws the sludge evenly from all parts of their path to the center tank discharge.

In the process of "continuous settling" there is maintained in the tank an upper zone of clarification and a lower zone of thickening, and just as long as the feed and discharge are at the same rate and other conditions remain constant, the relative height of these two zones will remain unchanged.

The following general rules governing the capacities of continuous thickeners hold true.

A. The clarification capacity is directly dependent upon the area of the thickener and independent of its height, except in cases where there is an increasing rate of settlement. (Discussed later under heading "Speed of Flocculation.")

B. The thickening capacity is directly dependent on the volume of the thickening zone and indirectly dependent upon the height, inasmuch as this volume for a thickener of predetermined area can only be affected by change in height.

A. Clarification Capacity: The more rapid the settling rate of the particles, the smaller the thickener area required, the relationship being expressed by the formula $A = \frac{4(F - D)}{3R \times Sp}$ in which

A represents unit thickener area in sq. ft. per ton solids. per 24 hours.
R represents settling rate in feet per hour.
Sp represents specific gravity of liquid.
F represents ratio of liquid to solids in feed.
D represents ratio of liquid to solids in discharge.

The derivation of this formula is easily understood if we consider a tank being fed with a suspension of dilution F and discharging a thickened product of dilution D, the initial settling rate of the particles in the clarification zone being at R ft. per hour.

Since there are F tons of liquid per ton of solids entering and D tons of liquid per ton of solids being discharged, there must be $F - D$ tons of liquid overflowing per ton of solids in the feed; or, stated in pounds, there would be $2000 \times (F - D)$.

Converting to volume in cu. ft. we have

$V = \frac{2000(F - D)}{62.5 \times Sp}$ = cu. ft. of liquid overflowing per ton solids per 24 hours.

It is evident that when the solids settle through a distance of R ft. the R ft. of clear liquid will be left behind and that in 24 hrs. at a rate of R ft. per hour, $24R$ ft. of liquid could be removed. We have already shown that the volume of this liquid in 24 hours would amount to $\frac{2000(F - D)}{62.5 \times Sp}$

Therefore the area required would be $\frac{\text{volume}}{\text{height}}$ or

$$A = \frac{2000(F - D)}{62.5 \times Sp \times 24 \times R} = \frac{2000(F - D)}{1500\ Sp \times R} = \frac{4(F - D)}{3\ Sp \times R}$$

B. Thickening Capacity: The volume capacity of a tank in the thickening zone for a specified moisture content in discharge

depends directly on the time or period of detention required for the sludge to reach this density, and may be determined from the following formula:

$$V = \frac{4T(G - Sp)}{3G(S - Sp)}$$

where V represents volume in cu. ft. required for thickening per ton solids per 24 hours.
S represents average specific gravity of thickened pulp.
Sp represents average specific gravity of solution.
G represents average specific gravity of solids in pulp.
T represents period of detention in hours.

Derivation of this formula is as follows:

The weight of solids in lb. in 1 cu. ft. of thickened pulp =

$$\frac{S \times 62.5}{D + 1}$$

where D represents the ratio of liquid to solids in sludge by weight.

Therefore, the cu. ft. of sludge containing 1 ton of solids would be:

$$\frac{2000(D + 1)}{S \times 62.5}$$

and on a basis of solids per 24 hours the volume for 1 hour would amount to

$$\frac{2000(D + 1)}{S \times 62.5 \times 24} \quad \text{or} \quad \frac{4(D + 1)}{3S}$$

and for a period of detention of T hours would be:

$$\frac{4T(D + 1)}{3S} = V$$

It can be shown that the following relationship exists between dilution and sp. gr. of the solution solids and pulps.

$$D = \frac{Sp(C - S)}{G(S - Sp)} \text{ and } D + 1 = \frac{S(C - Sp)}{G(S - Sp)}$$

substituting, we have

$$V = \frac{4T \times \frac{S(G - Sp)}{G(S - Sp)}}{3S} = \frac{4T(G - Sp)}{3G(S - Sp)}$$

Classification of Settling Problems.

It is readily seen that there are two distinct phases to every settling problem, one dealing with conditions meeting the desired clarity of "overflow" and one governing the requirements for proper moisture content in "underflow." Therefore from a practical standpoint "settling problems" may be grouped under the two broad heads of clarification and thickening.

I. CLARIFICATION.

In all clarification problems, area is generally the controlling feature, the aim being to obtain the lowest unit area (sq. ft. per ton solids treated) permissible with satisfactory operation, including a safe allowance for fluctuations in feed conditions, such as dilution, temperature, etc.

From the formula for area it is seen that the rate of settlement is one of the controlling factors, its relationship being expressed as follows: The area of a thickener varies inversely with the settling rate R, other conditions remaining constant. It is therefore apparent that any agency which will effect an increase in settling rate will bring about a corresponding reduction in tank area required. It is also evident that the determining factor in rate of subsidence is the settling rate of the slowest settling particles, which are those of smallest diameters. The problem then resolves itself into the control of the settling rates of the finest settling particles in a suspension and is governed by the same general principles that apply to colloids. With coarse particles, gravity is the controlling factor, but as the particles become finer and finer, the effect of gravity is gradually reduced and is eventually overbalanced by the forces of surface energy and Brownian movement, and a colloidal state is reached where the dispersed particles remain in permanent suspension in the liquid, in much the same manner as gas fills a container.

Although the physical properties of a colloidal solution are strikingly different from those of a suspension, the effects are due to difference in size of particle only and the consequent changing relationship of surface to mass involved. From a state of coarse suspension, through finer suspensions and colloidal solution to true solutions, there exists a perfect continuity in change of particle size, and the change from one state to another is not sharply defined.

The following classification taken from Zsigmondy is of value in giving a conception of the approximate range in particle size occurring in suspensions and colloidal solutions.

Classification of Solid Particles.

Suspension: Particles over 0.1 micron[3] in mean diameter.

Colloidal Solution: Particles between 0.1 and 0.001 micron in mean diameter.

True Solutions: Particles under 0.001 micron in mean diameter.

The pulps encountered in practice vary from coarse to fine suspension, in which are contained relatively small amounts of colloidal material, and rarely do we have to deal with a true colloidal solution. Probably the largest content of colloidal material is found in certain of the clays and in sewage and trade wastes. Nevertheless, where a clear overflow is desired, even the presence of a small amount of colloidal matter must be dealt with and is a controlling factor in the sedimentation of the total suspension.

Control of the Colloidal Content.

It is therefore of highest importance where possible to reduce the actual content of colloidal matter previous to sedimentation.

The total colloidal content of any material is affected by the following processes: mechanical treatment, chemical treatment, and heat treatment.

Mechanical Treatment: Since colloidal matter is due to the fine state of subdivision of the particles, the grinding and pulverizing of material previous to sedimentation are factors of extreme importance. A careful consideration of this phase of the problem will result in a minimum colloidal content.

[3] A micron is 1/1000th of a millimeter.

Where wet grinding is immediately followed by sedimentation, the old system of grinding to the desired fineness by one-pass through a ball or pebble mill is giving way to the modern method of closed circuit grinding, in which a classifier is run in closed circuit with the mill, giving a constant overflow of desired fineness and a continuous return of oversize back to the mill to be reground.

In the one-pass system the material must be detained in the mill until the largest particle in the discharge will pass through the required mesh, and it is evident that a considerable portion will be pulverized to a much finer state of division than required, whereas with the closed-circuit system the passage through the mill is more rapid and the material as fast as it is reduced to the proper size is removed together with a percentage of coarser material and conducted to a classifier where a separation is made into two products: an overflow of the desired mesh and an oversize which is returned to the mill for regrinding. With this system, the production of extreme fines is limited to those produced in a relatively rapid pass through the mill and therefore their content is proportionately less than where the one-pass system is used and the importance of proper control and regulation in grinding, as an agency in effecting minimum slime content, is readily seen.

Chemical Treatment: Where sedimentation forms a step in chemical processes the settling properties of the suspension are markedly affected by slight changes in methods of treatment. For example, in the manufacture of phosphoric acid in which tricalcium phosphate is treated with sulphuric acid, the insoluble calcium sulphate formed is removed by sedimentation. It has been found that the rate at which the acid was added had a pronounced effect on the size of the calcium sulphate crystals obtained and was therefore an important item in bringing about satisfactory settling. Similarly, in the first carbonation of sugar juices and treatment of hot saccharate, the speed and proper regulation of temperature have a marked effect on the settling qualities of the solids subsequently removed by sedimentation.

Many other examples could be cited showing the possibilities of effecting good settling properties by proper conditions and methods in preliminary treatment.

Because a material exhibits poor settling qualities is not sufficient ground for condemning its treatment by sedimentation without first making an investigation as to effects of certain changes in methods of preliminary treatment. In consequence, the problem of settling often involves the study of process treatment with the view of effecting favorable settling conditions.

Heat Treatment: Preliminary heat treatment of dry pulverized material is almost invariably attended with beneficial results in settling. In general material which has been dried or roasted settles better than when not so treated. While it would be impractical to employ this method for no other reason than to improve settling conditions, many cases are on record where the heat treatment employed as part of a necessary process has resulted in improved settling. In the treatment of Cripple Creek ores at the Golden Cycle Mill, Colorado, the pulverized material is roasted prior to cyanidation with marked improvement in settling qualities over unroasted ore.

Effect of Entrained Gas.

Gases may be present in a pulp either absorbed and occluded in the pores of the substance or adsorbed on its surface. The buoyancy of the entrained gas tends to hold up the particles and naturally interferes with settling. Samples of lithophone prior to calcining have shown the presence of adsorbed H_2S gas. Potash char from beet sugar factories contains particles of carbon with occluded gas. When treated with water for removal of potash, these particles refuse to settle. However, it was found by experiment that if the residue was brought to a red heat and plunged into water, the gas was driven off and the carbon pores were filled with water, with the result that the particles rapidly settled, leaving a clear overflow.

Another experiment was performed in which the residue was mixed with water and placed in a tight jar connected up with a suction pump. A copious supply of gas bubbles was seen to rise throughout the liquid and by vigorous shaking and application of suction all entrained gas was removed. Suction was then turned off, and a test showed that the material would now settle.

Occasionally we have to do with pulps where small quantities

of gas are being generated by chemical action within the pulp itself. Needless to say, such constant evolution of gas, if present only in minute quantities, interferes greatly with settling, by the rising currents produced. It is therefore of extreme importance that all gas generation be eliminated from pulps prior to the process of settling.

It has been found in the treatment of sewage, that the generation of gas is in a measure prevented by gentle agitation, with greatly improved results in subsequent sedimentation.

Mechanics of Clarification.

In all clarification problems dilution ratio or the ratio of liquids to solids has a most important bearing. If we pour a very thin pulp—for example, a greatly diluted metallurgical slime—into a glass cylinder and allow it to settle, we observe:

First—That a classification takes place, in which the coarsest particles settle to the bottom at a comparatively rapid rate, while the finest particles, settling at the slowest rate, remain on top, with gradation in size ranging between these limits. All the particles have free movement and excepting those of colloidal size, settle at a constant velocity, which is expressed mathematically by the formula of Stokes as follows:

$$U = \frac{2}{9k} r^2(d - d_1)g$$

in which U is the velocity, r is the radius of the particle, d and d_1 are the densities of the particle and medium respectively, g is the acceleration of gravity, and k is a constant depending upon the viscosity of the liquid medium.

Second—That a gradual clarification takes place, relatively slow in the last stages if very fine particles are present, and that there is an absence of any line of demarkation between the settling solids and supernatant liquid.

Now let us gradually increase the density of the pulp by added amounts of solids and note what happens after each addition when the pulp is well mixed and allowed to settle. We observe:

First—That a dilution is soon reached in which the fastest settling particles form into a zone and settle from thence on collectively and at a retarded rate.

Second—That this zone commences to form at progressively earlier periods until eventually a point is reached where the initial subsidence of solids is in mass, no independent particle movement being discernible, and proceeds with a sharp line of separation from the supernatant liquid.

Third. From this point, where the subsidence takes place more or less at a constant rate, a point in concentration is reached where there is a marked falling off in rate. This is called the point of compression, and marks the dividing line between the zone of clarification and the zone of thickening.[4]

Accordingly pulps may be classified as follows:

	Type	Character of Subsidence	Description	Examples
Clarification; free settling zone	Dilute	Independent particle subsidence	Particles or flocs settle independently. No definite line of subsidence. Settling unhindered. Settling rate mainly dependent upon size of particle or floc.	Turbid water sewage and trade wastes
	Intermediate	Phase subsidence	Upper zone of independent particle subsidence. Lower zone of collective subsidence. Line of demarcation not sharp.	Chemical and metallurgical pulps
Point of compression	Concentrated	Collective subsidence	Definite line of subsidence. Settling rate decreases with increasing concentration of solids. Settling rate retarded by particle or floc interference.	Chemical and metallurgical pulps
Thickening; compression zone	Compact	Compact subsidence	Flocs in intimate contact. Subsidence due to compression.	All pulps by sedimentation pass into this zone

[4] See "Methods for Determining the Capacities of Slime-Settling Tanks." H. S. Coe and G. H. Clevenger, Bulletin of the Am. Inst. Mining Eng., March, 1916, 597.

It is known that solid particles when suspended in a liquid are covered with a surface film of the liquid, the concentration of this film being dependent upon both the character of the adsorbing surface and the liquid medium. In the case of concentrated pulps, owing to the close approach of these surface films there is an apparent viscosity, which increases as the distance between particles becomes less and less until a point is reached where the particle films are in close contact. This increasing viscosity, with increase in concentration, offers greater and greater resistance to the passage of liquid which is being eliminated from the lower zones and may be likened to a process of diffusion. The effect of reducing this resistance by creating a free channel for the passage of the liquid is strikingly demonstrated in the following simple test:

A sample of pulp is placed in two test tubes. One is placed in vertical position and one is slightly inclined. In that one which is inclined, it will be noted that besides the increased clarification resulting from increased settling area, the pulp in settling away from the upper surface of the tube leaves an open channel which facilitates the free passage of the liquid. The rising current of the liquid on the upward surface and the settling of the solids on the lower are quite marked.

Although in the higher dilutions of concentrated pulps there may be considerable latitude of movement between individual particles permitting limited classification, their free movement is nevertheless impeded by particle interference, which increases rapidly at greater concentration. The particles, therefore, instead of settling independently as in dilute pulps, settle collectively, and individual movement is dependent upon the movement of adjacent particles.

Moreover, it has been noted that in a dilute suspension clarification takes place more or less uniformly throughout a zone of relatively great height extending from the top of the column to a point where the accumulation of settled particles at the bottom of the cylinder forms a surface line of demarcation. This line of demarcation rises as clarification proceeds, but may reach a maximum before clarification is complete and thereafter recede at an extremely slow rate due to a general consolidation or compacting of individual particles. Concentrated suspensions do not

show this zone of gradual clarification, but instead there is an immediate separation of clear liquid from the subsiding solids which increases in depth as settling continues. The effect is to a large extent mechanical, and is caused by enmeshing of the finest slow-settling particles in the matrix of subsiding solids which have become concentrated to the point where free particle movement is no longer possible. In practice, advantage of this effect has been obtained in a thickener by returning a portion of the sludge discharge back to the feed in the proper proportion to maintain a clarified overflow.

The concentrated type of pulp is generally met with in metallurgical and industrial chemical processes, while the dilute type is encountered in sewage, trade wastes and water clarification problems.

Theory of Colloidal Dispersion.

We have referred to the general conception of a colloidal state rather than to the limited idea conveyed by the term colloidal substance, and to the fact that any substance can be brought into the colloidal state if reduced to such a fine state of subdivision that the Brownian movement will keep the particles suspended in a liquid medium, provided the proper conditions prevail to prevent agglomeration and maintain stability. We have also emphasized the important consideration of the enormous surface involved as compared to the actual mass of the particles and its effect in bringing into play the forces of surface energy.

The most widely accepted theory in explanation of the stability[5] of the colloid is based on the assumption of an electric charge carried by the particle. This charge is not inherent in the particle or produced by any effects of frictional electricity, but is a surface phenomenon derived by virtue of preferential adsorption[6] of either positive or negative ions from dissociation of compounds. The particles if charged with like sign, *i. e.*, all positive or all negative, will be mutually repelled and remain dispersed through the liquid medium in permanent suspension and responsive to the bombardment effect of the Brownian movement.

The character and intensity of the charge for a given substance vary with the nature of the ions present and their selective adsorp-

[5] W. C. Lewis: A System of Phys. Chemistry, I, 362.
[6] W. D. Bancroft, Trans. Amer. Electrochem Soc., 27, 175.

tion by the substance, and are influenced by such factors as condition of particle surface, ion concentration, temperature, etc.

Flocculation.

In order to destroy this condition of stability and bring about precipitation, it is necessary to neutralize the charge on the particle by introducing a charge of opposite sign, either by the addition of an electrolyte or another colloid. Accordingly, negatively charged colloids are precipitated by positive ions and positively charged colloids by negative ions. The neutralized particles acted upon by the force of gravitation and assisted by the Brownian movement agglomerate into flocs, producing the condition known as flocculation.

It should be borne in mind that flocculation is not a specific term but applies to a general condition which is qualified by varying degrees, such as *intense flocculation, slow flocculation, etc.*

By flocculation, the suspension has been changed from a multitude of fine particles with correspondingly slow settling rates to a relatively small number of flocs which settle out at a greatly increased rate of subsidence, similar to particles of larger diameter. Flocculation not only brings about a removal of the dispersed colloids but materially increases the settling rate of the suspension as a whole, and its application to problems of clarification and sedimentation is readily seen. Its effect on dilute suspension is to increase the volume occupied by the solids, so that a concentrated condition is reached at much higher dilution than would otherwise be possible. The effect, therefore, of mechanically entrapping the finest particles is evidenced at relatively high dilutions. Similarly, flocculated pulps reach compression at higher dilutions than when not flocculated.

Owing to the fact that the colloidal content in most pulps is relatively low and that the main body of the suspension settles rapidly, a separation and removal of the colloidal portion with special treatment may result in large economy in total required settling area. Moreover the fact that flocculation applied to intermediate and concentrated pulps often converts them into compact pulps by virtue of the expansion effect of floc formation is another reason for separate treatment, for in the process of separation the colloids would be removed in a dilute pulp in which the

maximum settling rate occurring from flocculation would be free to exist.

In general, the methods for producing flocculation may be classified as follows:

1. Addition of electrolytes.
2. Addition of colloids—
   (a) By direct introduction.
   (b) By methods of precipitation.
3. Addition of colloid plus electrolytes.
4. Electric current.
5. Biological action.

1. Addition of Electrolytes: In the use of electrolytes the following rules in general hold true, and while there are a number of exceptions, their value as a guide in flocculation problems is recognized:

(*a*) Flocculation is affected by ions bearing a charge of opposite sign to that of the colloidal particles (Hardy's Rule).

(*b*) The flocculating power of electrolytes increases decidedly with the valency of the precipitating ions (H. Schultz's rule). The bi-valent ions are far more efficient than the univalent; tri-valent in turn still more effective than bi-valent.

(*c*) The highest degree of flocculation is attained at a definite range of concentration of electrolyte.

(*d*) Any increase in the amount of electrolyte, after reaching this neutral zone of precipitation, tends to reduce the degree of flocculation.

(*e*) The higher the concentration of the suspension in the liquid the less amount of a given electrolyte required per ton of dry solids, due to the fact that some of the electrically undischarged particles are entrapped in the large amount of neutral coagulum.

(*f*) The presence of small amounts of colloids belonging to the emulsoid group called protective colloids often interferes with flocculation and necessitates the addition of increasing amounts of electrolyte and often a different kind of electrolyte.

The sign of the electric charge on the colloid may readily be determined by methods of electrophoresis or by testing against

sols having a charge of known sign. To determine by electrophoresis, place the sol to be examined in the bend of a U-tube, filling the limbs with aqueous solution of a salt giving approximately the same conduction as the colloidal dispersion, into which dip electrodes connected up with some source of direct current, and note in which direction the particles migrate. If toward the cathode, or with the current, the charge is positive, if toward the anode, negative. A more convenient method consists in observing the direction of migration through a microscope, a drop of the liquid under examination being placed on a glass slide which is provided with platinum electrodes.

Burton gives the following classification of colloidal dispersions and suspensions:

Anionic (— Charge)	Cationic (+ Charge)
The sulphides of arsenic, antimony and cadmium.	Hydrates of iron, chromium, aluminum, copper, zirconium, cerium and thorium.
Solution of platinum, silver, gold or mercury.	Bredig solutions of bismuth, lead, iron and copper.
Vanadium pentoxide.	Hofmann's violet, magdola-red, methyl violet, rose neline-hydrochloride, Bismarck brown, methylene blue.
Stannic acid and silicic acid.	Albumen, haemoglobin, agar.
Aniline blue, indigo, molybdena blue, soluble prussian blue, eosin, fuchsin.	Titanic acid.
Iodine, sulphur, selenium, shellac, resin.	
Starch, mastic, caramel, lecithin, chloroform.	
Silver halides.	
Various oil emulsions.	Diatoms, unicellular.
Amoebe and animal microorganisms.	Algae and vegetable microorganisms.

In electrolytes, the cations, or positive charged ions, are hydrogen and the metals, the acid radicle being the anion, and showing negative charge. The effect of the valency of the ions on the charge is shown by the subjoined table of results by Freundlich,

which gives the minimum concentration of electrolyte to produce coagulation of the negatively charged As_2S_3 sol, the electrolyte concentrations being given in millimoles per liter.

KCl 49.5	HCl 30.08	$Ba(NO_3)_2$ 0.687
KNO_3 .....50.5	$MgCl_2$ 0.717	$AlCl_3$ 0.093
NaCl 51.0	$CaCl_2$ 0.649	$Al(NO_3)_3$ 0.095
LiCl 58.4	$BaCl_2$ 0.691	

It is apparent that the quantity of electrolyte required depends only upon the cation, and that a striking difference is shown between cations of different valency.

The protective effect[7] of various emulsoids varies between very wide limits. Among emulsoids of most common occurrence may be mentioned gelatine, soap, gum, albumin, casein and isinglass.

In the clarification of industrial waste water, the presence of one or more protective colloids is often encountered; as, for example, the discharge waters from silk mills, which contain considerable quantities of gums and soap.

Many examples of the application of electrolytes to flocculation are to be found in practice, among which may be mentioned use of aluminum sulphate and alums in water clarification, settling of metallurgical slimes by addition of $Ca(OH)_2$, and the use of $Al_2(SO_4)_3$ and H_2SO_4 in settling of clays.

From a practical standpoint, the choice of an electrolyte is not alone a question of determining what is the most effective flocculating agent for a given material, but is often governed by one or more of the following requirements:

1. It should be inexpensive.

2. It should have little or no detrimental action on either the solids or the liquid under treatment.

3. It should not introduce reagents which would be deleterious to subsequent treatment.

4. It should permit of a low moisture content in thickened sludge.

2. Addition of Colloids.[8] (a) *By Chemical Precipitation.*

This method of flocculation is of quite common occurrence in the clarification of sewage and trade wastes and is commonly

[7] W. D. Bancroft, Jour. Phys. Chem. (1915), 19.
[8] W. D. Bancroft, Journal Physical Chem., 18, 555.

known as "chemical dosing." The reagents most frequently met with are lime and alum, or lime and ferrous and ferric sulphate, forming precipitated $Al(OH)_3$ or $Fe(OH)_2$ and $Fe(OH)_3$ as the case may be, substances which contain relatively high positive charges when in the colloidal condition, which condition is attained at the instant of precipitation.

(b) *By Direct Introduction.* This method, while easily demonstrated in the laboratory, is only occasionally met with in practice. Examples are the use of manure in the settlement of caliche slime in the nitre field of Chile; also the use of glue and certain organic colloids in the flocculation and settlement of colloidal precipitates encountered in chemical processes. Research on the use of certain colloidal clays and colloidal waste products gives promise of large practical application to special cases of flocculation where the use of electrolytes would be prohibited, due principally to the high salt concentration of the liquid medium.

3. Colloids Plus Electrolyte: A colloid together with an electrolyte which will flocculate it, when added to a suspension under certain conditions, will result in a complete clarification of the suspensoid. In the laboratory this has been demonstrated in a number of cases. For example, the material under treatment contained silk gum or cerisin in a colloidal condition, which was required to be removed. This was accomplished by adding a small amount of clay, mixed well with the solution by shaking and then adding enough acid to flocculate the clay, which resulted in complete clarification of the liquor. To all appearances, the flocculation of the clay produced nuclei to which the primary colloidal particles gathered. It seems reasonable to suppose that this condition was due to adsorption by the clay particles and the mechanical effect caused by a large body of flocs entrapping the finest particles like a filter mat, bringing everything down with it.

4. Electric Current:[9] The method of producing flocculation and increasing settling rates by passing an electric current through a suspensoid is commonly referred to as "electric settling," and has been employed in treatment of sewage.[10] Preliminary investi-

[9] A. W. Fahrenwald: "Testing for Flotation Process," 53-64.
[10] A. M. Williamson, Trans. Amer. Electrochem. Soc. (1915), 27, 193.

gation of the subject by passing the current from a 110-volt electric light circuit, both alternating and direct current, through various pulps using electrodes of copper, zinc, aluminum, iron and carbon, gave the following results: No flocculation was produced in either alkaline or acid pulps when carbon electrodes were used. Flocculation was produced in every case when metal electrodes were used. Usually it was necessary to acidify slightly the pulps, but in some cases strong flocculation was exhibited in alkaline pulps. The general inference from these preliminary tests was that the electric current alone was not directly responsible for the flocculating effects produced, as demonstrated when carbon electrodes were used, but when soluble metal electrodes were used electrolytes were formed which, in themselves, produced flocculation. In other words, the effect of electric current on flocculation is indirect, and the same results are possible by the introduction of electrolytes.

As mentioned, these tests are only preliminary to more extensive research, and it is possible that further investigation, introducing varying conditions as to temperature, current density, arrangement of electrodes, etc., will result in a method of flocculation by the direct effect of electric current.

5. Biological Action: Under certain conditions bacterial growth will bring about a condition of flocculation. The propagation by splitting up and colonizing has the effect of producing flocs or aggregates of bacteria which, as active centers, digest the colloidal organic matter and effect clarification.

A striking illustration is the treatment of sewage by the activated sludge method. Briefly, this method has to do with the fact that certain bacteria (aërobic bacteria) require oxygen for their existence and in a properly aërated sewage they will thrive and propagate, whereas the other class (anaërobic bacteria) will die off or become dormant in this atmosphere. These aërobic bacteria rapidly multiply and form colonies (aggregated of bacteria) which in their growth feed on the organic matter in suspension and not only bring about clarification but change the chemical composition of the sewage through a process of nitrification, so that a stable effluent is obtained.

Temperature.

Temperature is one of the most important and widely-used agencies for improving the settling qualities of a pulp. Even slight increases in temperature are attended with marked increase in settling rate, and oftentimes pulps which settle so slowly that excessive tank areas would be required are placed in the sphere of successful sedimentation by the simple expedient of raising the temperature. This is particularly evident in pulps where the liquid medium is a concentrated salt solution or in liquid where a pronounced reduction in viscosity occurs with increase in temperature. While in general the results are attributed to reduction in viscosity of the liquid medium, in some cases the degree of flocculation is improved and may even be brought about by temperature alone.

Examples in practice where improved settling has resulted from increase in temperature conditions are numerous, and the clarification of sugar juices after first carbonation is a notable example where temperature is a controlling factor in effecting satisfactory sedimentation. In this case the critical temperature is in the neighborhood of 85° C., where good settling prevails. As the temperature falls off there is a marked decrease in settling rate, and at 55° C. the rate is practically nil. The effects are due to a change both in viscosity of the liquid medium and in the degree of flocculation.

Physical Character of Flocs.

Flocs are encountered which are compact and approach a spherical form, having more or less of a granular appearance, others are long, stringy coagules of no definite shape, and between these limits are all gradations of form and physical character. It is evident that the granular flocs will have better settling properties than the stringy ones, but how to obtain this most desirable floc form is a matter which apparently has been little investigated.

The introduction of foreign substances, such as pulverized limestone, seems to exert a beneficial effect in some cases in furnishing a nucleus about which the floc builds in a more or less compact or spherical form. By adding substances of high specific gravity, such as barium sulphate, for floc nuclei to "weight" the flocs, the rates of settling may be materially increased in certain

types of dilute suspensions, where the solids are largely present in colloidal form.

Speed of Flocculation.

The speed of flocculation varies considerably. In some cases it is most energetic and the flocs reach their full growth in a very short space of time, and in such cases it is usual to find well-formed compact flocs. On the other hand, a slow growth tends to form stringy flocs—evidently due to the effect of gravity over the period of growth—and is more noticeable in liquids of low viscosity than of high viscosity, and would undoubtedly be affected by varying degrees of surface tension. Suspensions which exhibit a rapid rate of flocculation settle at a more or less uniform rate, whereas those which form slowly show a gradually increasing rate of settlement in conformity with the floc growth.

It is apparent that if a pulp showing the slow growth of flocculation were placed in a tank, the determining rate for a continuous overflow of clarified effluent would be the rate observed at the end of a period of time required for a particle to pass from the center of the tank to the overflow, and advantage of the maximum rate of settlement which might occur at the end of an hour's period could be obtained only by allowing a corresponding period of detention in the tank before overflowing. It is possible to attain this condition in a thickener by submerging the feed-well a proper distance to give detention capacity, and with due regard for proper distribution and elimination of short circuits.

Removal of Colloids.

In many cases not a clear overflow is wanted, but an overflow containing the finest particles in suspension. In the flotation process for treating ores it often happens that the presence of colloids, particularly primary slime, not only has a detrimental effect, but may totally prevent good recoveries, and its removal is therefore of greatest importance.

In a number of ores it is known that the primary slimes are barren of values, and it is apparent that in this class of ores a removal of this waste material in the early stages of ore dressing would be of great benefit not only in reducing tonnage of material handled but in the removal of substance which might prove deleterious in subsequent operations.

Deflocculation.

In effecting these separations a condition of dispersion or deflocculation is of utmost value, allowing for a greater difference in settling rates between the fine sizes, and therefore a more perfect separation. The methods of deflocculation are covered by the same general principles that govern flocculation, and it becomes a question of testing out each particular material to determine the proper deflocculating agents.

In the refining of clays, Na_2CO_3 and NaOH are used in a number of cases in effecting a dispersion of the clay particles and permitting the sand particles to settle out and be removed. However, some clays are flocculated by these reagents; there is a very wide difference in the action of electrolytes on various clays, and no general rule as regards deflocculating agents can be given.

The ions of hydrogen and hydroxyl are very strongly adsorbed by certain substances, and in certain cases overshadow the effect of ions that accompany them. The deflocculating effect of NaOH is attributed to the strong adsorption of the negative hydroxyl ions by the already negative-charged clay particles. In the case of sodium silicate the effect is attributed to its hydrolizing into sodium hydrate and colloidal silicic acid, both of which carry negative charges.

The same rules that apply to flocculants regarding the concentration of electrolytes apply likewise to deflocculants, and it is possible to bring about flocculation after reaching a condition of deflocculation by continued addition of electrolytes. In some cases deflocculation may be brought about by the use of such agents as molasses slop (a by-product from the manufacture of cane sugar) and various other organic colloids.

II. THICKENING.

Mechanics of Thickening.

There is a remarkable difference in the thickening properties of various pulps. Some consolidate within a few hours to a dense sludge that will barely flow through a pipe, whereas the moisture content of others settling for days will not be reduced below 95 percent. These effects are largely due to differences in specific

gravity of the solids, and physical character and structure of the flocs.

The process of thickening starts from the bottom of a tank and progresses upward, the limit of the thickening zone being reached at a point where the particles or flocs just begin to touch one another.

If we fill a cylinder with well-mixed free-settling pulp and allow it to settle, it is evident that at commencement all the pulp will be of the same consistency and therefore free settling will progress as one zone, but as settling continues there is a gradually increasing concentration of particles in the lower portion of the cylinder, so that simultaneously with the free settling of the upper levels a gradual consolidation or thickening is taking place in the lower levels. This zone of compression or thickening continues to rise until it totally involves the zone of free settling.

The merger of the two zones is observed by a slowing up in rate of subsidence, and has been referred to as the point of compression. Subsidence from this point on is effected by a gradual consolidation of particles in the lower portion of the zone by compression from weight of particles overlying. The liquid being removed by displacement is forced upward along channels of easiest resistance, the channels becoming more constricted as thickening progresses. Subsidence continues, but at a greatly reducing rate, and eventually stops when an equilibrium in forces is reached; this point is called the point of final density for straight subsidence. In other words, the zone of thickening has consolidated into a zone of minimum moisture content.

A tall cylinder will show a deeper zone of final density than a low cylinder, the depth of zone being in almost direct proportion to the height of the pulp columns at the start of thickening and likewise varies directly with the time. However, the average density for the s a m e d e p t h of zone is a direct function of the time and independent of the height of the original thickening column.

For example, if a pulp column measured from the point of compression is 12 in. (30 cm.) high and settles to 2 in. (5 cm.) of final density in 12 hours, one 24 in. (60 cm.) high will after 12 hours show the same density for 2 in. (5 cm.) in height, but

will require approximately twice as long a period before the total solids are of final density, the zone of which will be approximately twice as high. Therefore, it may be stated that for a certain height of thickened pulp, the density is directly dependent upon the time and independent of the height of the tank over and above that required for the necessary detention capacity.

It is true that with deep tanks the additional weight of the higher column of solids tends toward greater consolidation than would occur in a shallow tank, but off-setting this is the greater resistance offered to elimination of water by constriction of channels, and as a result no practical advantage is secured by making tanks deeper than 10 ft. to 15 ft. (3 to 4.5 m.).

It has been found, however, that the slow turning over and mixing of the particles by mechanical raking result in a considerable lower final density than is obtained by straight compression alone, due to the breaking down of floc structure and the adjustment of different size particles to accommodate the smallest volume. This can be easily demonstrated by taking a pulp which has reached final density by natural subsidence, and noting where the pulp line comes, and then stirring with a glass rod, very slowly, allowing it to subside again, to final density, when the level of pulp surface will be seen to be lower than that first recorded.

In general, while free settling rates are increased with the degree of flocculation, requiring correspondingly smaller tank areas, the process of thickening is retarded in the same degree and where an ordinary settling box is used the final density obtained would be proportionately less. The action of the rakes in a continuous thickener, however, counteracts this effect, with the result that much higher densities are obtainable than without this mechanical action.

Channelling by Artificial Means.

Research has shown that rapid vibrations of low amplitude of vertical wires arranged in a tank will hasten thickening by mechanically assisting channelling and giving greater facility for upward passage of liquid. The use of suspended rods and corrugated sheets in a tank to assist channelling has been tried out in some cases with certain improved results. Mechanical difficul-

ties, however, have not warranted the practical application of these methods to continuous settling.

Endosmose.[11]

Endosmose or electric osmose denotes the movement of a liquid through a membrane by the application of an electric current. If water be placed in a vessel divided in half by a vertical porous membrane, and an electrode be placed in each half, then the water will move through the membrane under influence of a direct current applied at the electrodes, so that the water-level rises in one compartment and falls in the other.

In applying endosmose to the thickening of pulps, the solids are prevented from movement by suitable means, such as a screened compartment, and may be considered to act as a diaphragm, the liquid being transferred from the solids by application of direct current in the proper direction between the electrodes. In this manner it is possible to remove a certain content of moisture and effect a thickening of the pulp. It is impossible to carry the action to the point of drying the solids, for a stage in thickening is reached where the force of endosmose is counteracted by the physical forces acting to retain the moisture and prevent further transference of liquid, and the final moisture content obtained is what might be expected by an ordinary filtration process.

Count Botho Schwerin has taken out a large number of patents on the use of endosmose as applied to thickening or dewatering of various substances.

One example is the dewatering of a peat mixture containing 85 to 90 percent moisture in which it is claimed that three-fourths of the water can be removed at a cost of only one-fifth of the energy available from the combustion of dried peat. The process has been only partially successful, owing mainly to failure to obtain a moisture content below 65 percent.

In general the method of thickening by endosmose is still in the experimental stage and offers considerable promise as a practical means of reducing the moisture content in those substances —for example, clays—which are particularly difficult to filter.

[11] T. R. Briggs, Jour. Phys. Chem. (1919), 21, 198.
W. D. Bancroft, Trans. Amer. Electrochem. Soc. (1912), 21, 233.

TESTING.

The most satisfactory testing is performed on freshly taken samples, with exact duplications of conditions that would occur in practice. Owing to the complexity and variation in conditions controlling each settling problem and the lack of exact quantitative methods in dealing with the various forces which affect flocculation and dispersion, it is impossible to formulate any exact methods of procedure; each case is a problem requiring independent study and analysis. Technical knowledge, experience, and sound judgment are essential in bringing about the effective solution, and while a certain systematic line of investigation is desirable it must be flexible enough to meet the changing conditions encountered with each problem.

SUMMARY.

The introduction of "continuous settling" has resulted in greatly increased application of sedimentation processes.

The practical requirement of every settling problem involves two distinct processes, one clarification, the other thickening.

The requirements for clarification are the minimum thickener area permissible with a continuous overflow of liquid of specified clarity.

The requirements for thickening are a continuous discharge of thickened pulp of lowest permissible moisture content.

In clarification problems the settlement of the finest particles is the governing feature.

The settling properties of a pulp may be largely improved by a proper adjustment of conditions in processes prior to sedimentation.

Flocculation is an effective method for increasing settling rates except in certain concentrated pulps where the expansion effect of floc growth brings the flocs in close contact, in which state settlements can occur only by compression of flocs.

Flocculation retards the process of thickening, causing increased periods of detention and a lower final density, although the moisture content of the final discharge is effectually reduced by the action of the rakes in a thickener breaking down the floc structure.

The beneficial effects of increased temperature, well recognized in metallurgical work, are shown to hold true for practically all pulps and are particularly pronounced in those where the liquid medium is of relatively high viscosity, and the successful issue of many problems depends upon the proper control of this one condition. Unlike flocculation, it exerts no deleterious effect on thickening and is oftentimes of assistance.

Each settling problem is governed by specific conditions requiring independent study and analysis, and the most satisfactory solution often involves a study of processes and methods with a view of possible changes in certain conditions, so as to alter the physical character of the suspension and promote improved settling.

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DISCUSSION.

W. D. BANCROFT[1]: There is one point I would like to bring up. It was known before that dilute colloidal solutions settled cloudily and that more concentrated ones settled with a clear liquid at the top, but so far as I know, nobody has offered any explanation of that until this paper of Mr. Deane's, where he points out that if you have a relatively high concentration, the coarser particles, in

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settling, strike against the fine particles and entangle them and carry them down; in other words, you are getting a sort of filtration effect. This is interesting because we get the same sort of thing in another case to which this same explanation can be applied. It is known that cream rises more rapidly and more completely in a deep pan than it does in a shallow pan, which is exactly the opposite, of course, of what one would naturally expect. It seems to me that this is merely the same thing, that Mr. Deane has been explaining to us, except we are getting upward filtration instead of downward filtration. People who have studied the settling of colloidal solutions in the laboratory have been very much puzzled by the fact that these have formed into layers; there will be a clouded layer and a clear layer, so that you get a banded structure. It seems to me that it might be possible that you get your clear structure when the concentration has gone far enough so that you are beginning to get this filtration effect, and it is quite possible to apply this same point of view that Mr. Deane has outlined to those things which are a hopeless puzzle. It is not merely a question of science helping out industry, but of technical results being of great importance and enabling us to clear up the purely scientific problems.

W. A. DEANE (*Communicated*): In connection with the idea of upward filtration which Dr. Bancroft has commented upon, I would like to point out some examples shown in practice.

In the purification of cane sugar juices by continuous settling in tray clarifiers it has been demonstrated that the clearest liquors are those drawn from below the top compartment.

The tray clarifier is a tank, with peripheral overflow weir, within which is suspended an inverted flat-cone diaphragm separating the tank into an upper and lower compartment, or there may be several of these diaphragms or trays, superimposed one above the other about two feet apart and each having a point of central discharge for thickened sludge and an overflow pipe for carrying off the clear supernatant liquid. The feed enters at the top compartment and passes in multiple to all trays, and by virtue of its mixture with each successive tray discharge takes on a higher concentration (or lower ratio of liquid to solid), resulting in a clearer overflow from the trays than from the top compartment. This filtration effect is due to the entrapping of the finest particles

in the denser matrix of readily settleable solids, and is observed when a definite or critical point in dilution is reached. Above this point the overflow is turbid and below this point it is clear. Further concentration has the disadvantage of retarding the settling rate without increasing the clarity of overflow. The example cited is typical of all tray thickener operation.

Referring to Dr. Bancroft's illustration of cream rising more completely in a deep pan than in a shallow one brings up another point: As I see it this effect is not due to concentration, because the dilution of the milk in both pans is the same, but may be attributed to the greater distance for filtration offered by the deep pan. This phase in clarification is illustrated in practical operation of a continuous sedimentation tank or thickener where a clearer overflow is obtained by increasing the submergence of the feed well the proper amount.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

GRAPHITIC ACID—A COLLOIDAL OXIDE OF CARBON.[1]

By Geo. A. Hulett[2] and O. A. Nelson.[3]

Abstract.

The history of investigations on graphitic acid is given *in extenso,* followed by a record of experiments to determine the vapor pressure of the water from this product at different temperatures. The extensive experimental and chemical work points to the water given off as having been simply adsorbed water, and not due to chemically combined hydrogen, while the basic substance is a solid carbon oxide of a colloidal nature in extremely thin plates of approximate formula C_3O or $C_{11}O_4$. [J. W. R.]

HISTORICAL.

Graphitic acid was first prepared by Brodie in 1859 by prolonged treatment of graphite with a mixture of $KClO_3$ and HNO_3 in the presence of sunlight. (Phil. Trans., **149**, 249.) The reaction took place slowly with no noticeable change in the graphite except an increase in weight which was observed after the action had apparently ceased. The substance was then thoroughly washed with water, dried, and again subjected to the oxidizing mixture until the reaction again stopped and there was a further increase in weight. Brodie found that it was necessary to repeat these experiments four to six times in order to arrive at a definite end point. By this time the product was lemon yellow in color, apparently crystalline, and practically insoluble in any known solvent. Dried at 100° C. and analyzed, the results indicated its formula to be $C_{11}H_4O_5$. Moistened with water it showed a slightly acid reaction toward litmus. Shaken with a

[1] Manuscript received March 16, 1920.

[2 and 3] Laboratory of Physical Chemistry, Princeton University.

solution of $Ba(OH)_2$ it took up barium, and Brodie obtained two products which he analyzed and to which he assigned the formulas $C_{11}H_3BaO_5$ and $C_{22}H_7BaO_{10}$. When this graphitic acid

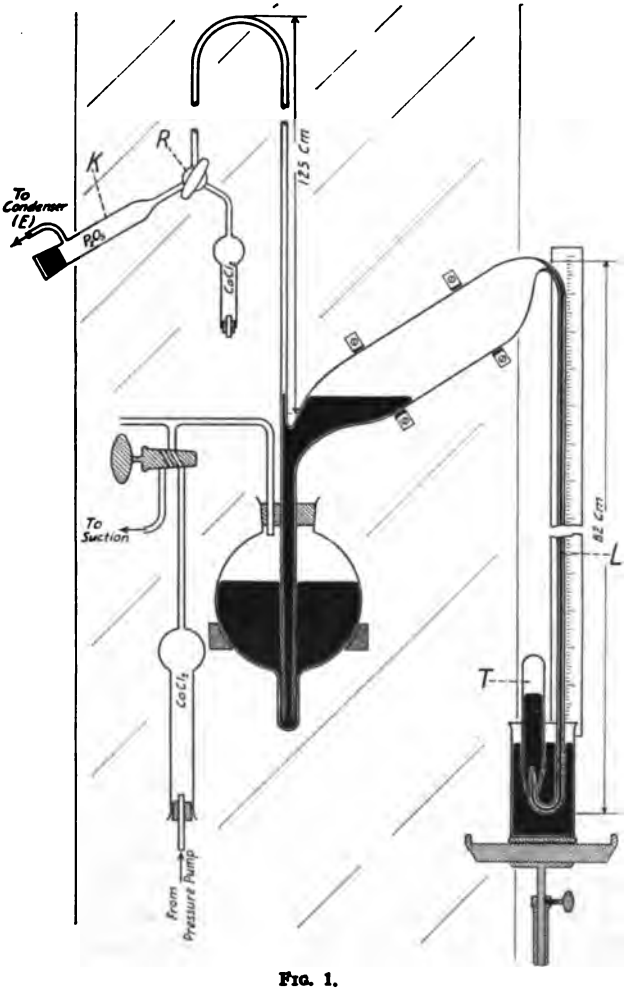

FIG. 1.

was shaken with reducing agents, *e. g.*, alkali sulphides, stannous chloride, etc., it turned black with a liberation of carbon dioxide. With ammonia it formed a colloidal solution that was readily coagulated by the addition of mineral acids.

Subsequently considerable work has been done by different investigators upon this subject, but not very much additional information has been obtained. Staudenmeier (Ber. Berichte, 1898, **31**) found that while a mixture of HNO_3 and H_2SO_4 had no action on graphite, that if $KClO_3$ was slowly added to the mixture, with continuous stirring, he could change the graphite into a green product by a single treatment, and this after washing, drying and further treating with $KMnO_4$ was readily changed into the lemon yellow graphitic acid. This was a decided improvement over the Brodie method in that the necessity of washing, drying and repeated treatment with $KClO_3$ and HNO_3 was eliminated, thus the process was shortened considerably, and also in that he could prepare large quantities without danger of explosion.

Berthelot and Petit (Ann. Ch., 1870 [4], **19**, 401; and 1890 [6], **20**, 20) carried out a long series of experiments on graphitic acid from different kinds of graphites, with the idea of getting some evidence on the nature and structure of graphite. These investigators observed that the products they obtained were noticeably hygroscopic after having been dried at 110° C. Upon analysis, after having taken special precaution to protect the product against moisture, they obtained a variety of formulas depending upon the graphite used. Thus from Ceylon graphite they obtained results that indicated the formula $C_{14}H_4O_7$, while from many of the other graphites products were obtained that usually showed less hydrogen. It is to be noticed that the formula ascribed to the graphitic acids by Berthelot and Petit are lower in hydrogen than are those suggested by Brodie. This is probably due to the fact that the former dried their products at 110° C. instead of at 100° C. as did Brodie.

Charpy (C. R. 1919, **148**, 920) attempted to prepare the graphitic acid by using permanganic and chromic acids as oxidizing agents, but found that the reaction very readily proceeded too far. Thus with a mixture of permanganate and concentrated sulphuric acid he was able to change most of his graphite into graphitic acid at ordinary temperatures, while with an increase in temperature to 40° C. some of the graphite was changed to carbon dioxide, and with a temperature of 100° C. half of the weight of the graphite was oxidized to carbon dioxide. With

chromic acid the same results were obtained at 45° C. as at 100° C. with permanganic acid.

Moissan observed that with anhydrous HNO_3, $KClO_3$

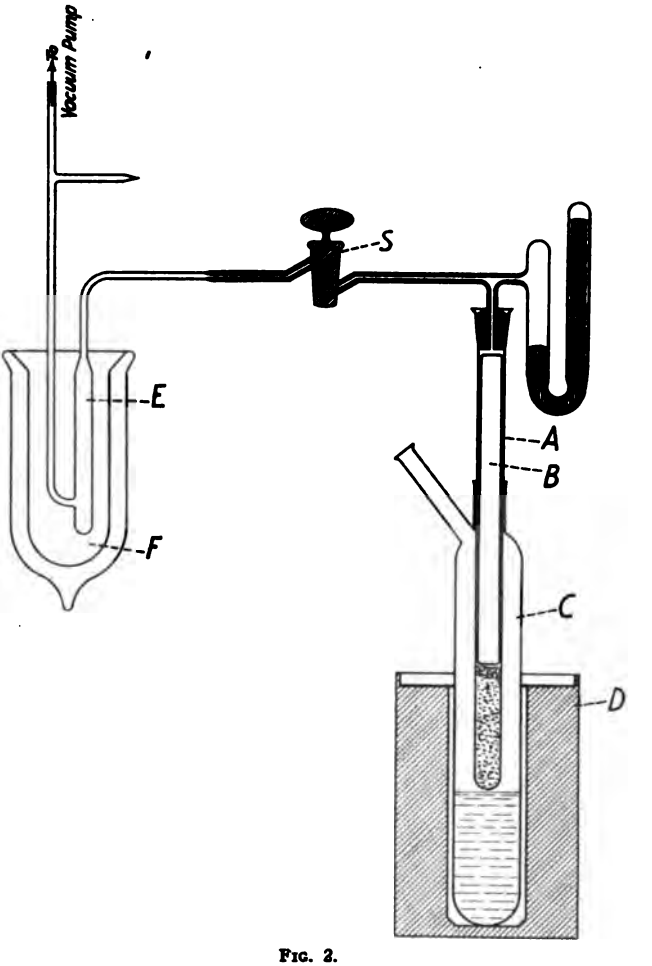

FIG. 2.

formed an orange-red solution which at 60° C. was very potent in transferring graphite to graphitic acid, but a trace of water retarded the reaction and prevented the formation of the orange-red solution.

Kohlschütter and Haenni (Zeit. anorg. and alle. Chem., **105**, 125) concluded that chlorine dioxide was the active oxidizing agent in the mixture originally used by Brodie. With a mixture of potassium chlorate and sulphuric acid, however, they were able to obtain only traces of graphitic acid at ordinary temperatures, while on heating the mixture to 40°–60° C. the reaction took place with explosive violence. Thus they were unable to obtain the desired results without the presence of nitric acid. But in view of the fact that HNO_3 alone or with H_2SO_4 is quite incapable of oxidizing graphite to graphitic acid, which is in perfect agreement with the works of Staudenmeier, they concluded that HNO_3 plays the mechanical rôle of facilitating the entrance of ClO_2 into the flakes of the graphite.

Luzi (Ber. Berichte, **24**, 4085; **25**, 214) has shown that natural graphite when moistened with concentrated HNO_3 and then heated, swells, forming little worm-like or dendritic products. Moissan (Ann. Ch. et de Phys. [7], **8**, 289, 306 and 466) repeated these experiments and found that graphite that had been treated with HNO_3 gave off at red heat nitrous fumes and a little CO_2, with a rapid swelling of the mass. He concluded this to be due to liberation of gases between the plates of graphite. This phenomenon was found to hold for all natural graphites, also all the graphites prepared by dissolving carbon in hot molten metals showed this swelling, while graphites made by simply heating amorphous carbon or diamond to very high temperatures did not show it.

Evidently NHO_3 has the peculiar property of penetrating between the flakes of graphite and also of dissolving $KClO_3$, so it seems to form a medium for rapid formation of graphitic acid from graphite. Furthermore, from this viewpoint it is easy to understand how an accumulation of KCl and other products between the flakes of the graphite slow up the reaction, and that little further action is possible until these substances are removed, by extraction with water and drying, when the reaction starts vigorously again. Possibly also some water is needed in the reaction.

Messrs. Selvig and Ratliff of the Bureau of Mines (Bulletin on: "The Problem of Determining Graphitic Carbon") find that by the Staudenmeier method Ceylon graphite may be transformed

to graphitic acid with a loss of 1.1 percent of the carbon as oxides and colloidal oxidation products. Acheson graphite lost 3.5 percent, Alabama graphite 12.8 percent, and a Pennsylvania graphite 17.8 percent. Most of this loss was found to have been as CO_2 during the reaction, with a trace of CO, and evidently a small amount of carbon was lost as colloidal oxidation product in the

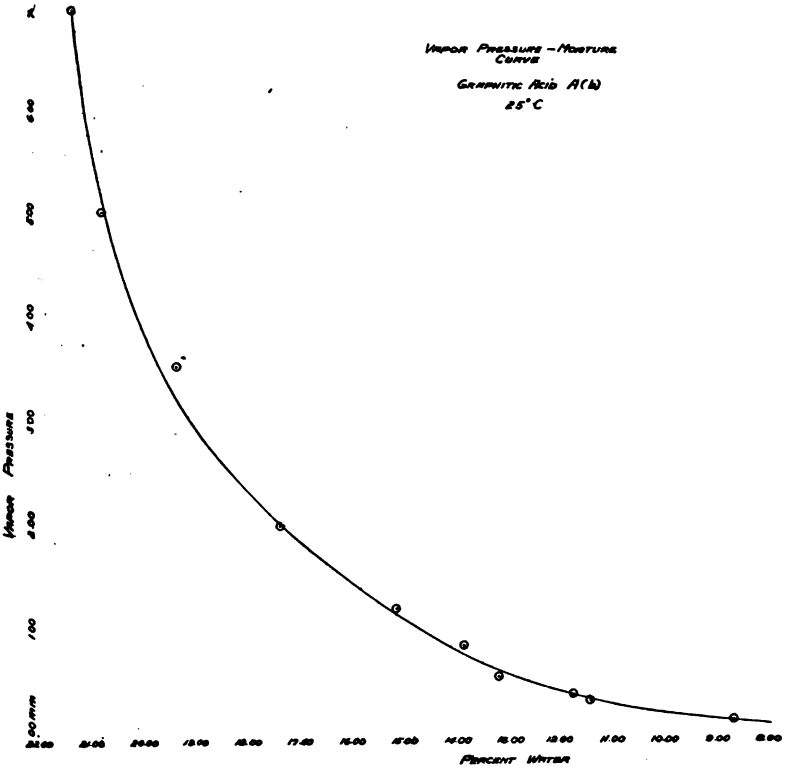

FIG. 3.

liquids used. The Brodie method showed from 1 to 2.5 percent greater losses with above graphites. It would therefore seem that, in the wet way, graphite goes through a series of stages of oxidations ending in CO and CO_2, and is never quantitatively changed to graphitic acid, although this appears to be one important stage in the process. Thus the conditions for producing the maximum graphitic acid, *viz.*, the oxidation potential, HNO_3,

water, temperature, etc., appear to be restricted to very narrow limits.

The beautiful yellow-colored flakes of graphitic acid are not crystalline, as shown by polarized light. Thiessen (U. S. Bureau of Mines) has observed that these flakes are made up of an infinite number of excessively thin plates, with a diameter of only 10 to 50 $\mu\mu$, and with a thickness less than the vision of the ultramicroscope. These particles show the Brownian movement very markedly, and a series of scintillations which is evidently due to reflection from the flat sides, only disappearing when the edges are turned to the line of vision. Evidently we have here a colloidal substance with an excessively large surface.

Our work on graphitic acid is the result of an effort to supplement some work in progress at the Pittsburgh station of the Bureau of Mines. Messrs. Selvig and Ratliff of that Bureau (*l. c.*) were working on the problem of determining graphitic carbon in electrodes, and had prepared a great variety of graphitic acids from Ceylon, Alabama, Pennsylvania, and Acheson graphites, as well as from carbon electrodes. The combustion analysis of these products presented peculiar difficulties due to their explosibility; furthermore, the results, aside from the percent of carbon, could not be interpreted owing to lack of knowledge of their moisture content. The air-dried products gave entirely different relations of C, H and O compared to the products dried at 100° or 110° C., as has been the practice of previous workers. Balbiano (Bull. Soc. Ch. de France, (1916), 194) has found that the dried substance is very hygroscopic, even in an atmosphere of 50 percent humidity. When placed in a vacuum over sulphuric acid there is a rapid loss of water at first, then its moisture is given off more slowly. A sample which had been dried for several months over H_2SO_4 was not constant, but showed an additional loss of 1.08 percent in the succeeding three months, and a further loss of 1.00 percent in a year. This is a characteristic behavior of moisture in organic and colloidal substances, but, as has been observed by many investigators, even our best dehydrating agents are incapable of removing all the moisture from colloids.

With the object of obtaining some information as to the moisture contents of these substances, we undertook an investigation of the graphitic acids prepared at the Bureau of Mines by Messrs.

Selvig and Ratliff, by the method we have used for determining the true moisture content of coals (Am. J. of Sc. **40**, 175), and which we have also applied to grains and cereals. (J. Ind. and Eng. Ch., Jan., 1920.)

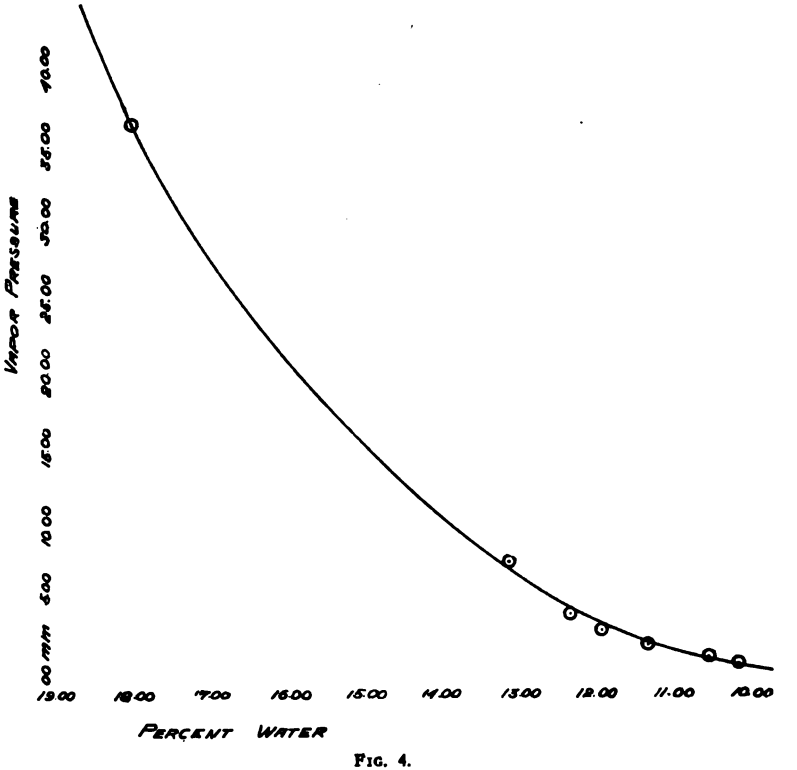

FIG. 4.

This method consists in heating the substance in a vacuum at a constant temperature. The moisture is condensed as ice in a U-tube at the temperature of solid CO_2 (— 78°), while the other gases are pumped off with a Topler mercury pump. At a given temperature, say 110° C., a colloidal substance gives off moisture and absorbed gas, rapidly at first, then at a decreasing rate, and in a few hours the evolution entirely ceases. These observations permit us to plot the percent moisture-temperature curve which became flat or parallel to the time axis, and they show the percent

of moisture obtainable at the particular temperature used. At a higher temperature a similar curve is obtained, but the flat part lies above the lower temperature curve, and at successively higher temperatures greater percents of water are indicated. Finally a temperature is reached at which there is no flat part but a continually increasing percent of water with time, showing unmistakably water of decomposition. A plot of all the results allows us to determine the point of temperature and time at which decomposition becomes measurable, and by extrapolation we get an idea of the moisture content of the substance. Some results on graphitic acid from Ceylon graphite, air dried, follow:

Sample A (a).

Temperature	Time of Heating	Percent Water	Total Moisture	Vol. Gas per Gram
Room	3¼ Hrs.	10.65	10.65	.....
100° C.	2 "	5.85	16.50	0.11 cc.
110° C.	3 "	0.38	16.88	0.39 "
165° C.	1¾ "	0.36	17.24	0.47 "
184° C.	1¾ "	0.41	17.65	1.70 "
218° C.	¼ "	(Exploded)		

The experiment ended in an explosion that wrecked our apparatus. The results showed, however, that large amounts of water could be removed from the graphitic acid with little decomposition, although at 184° C. there is a marked increase in the gases liberated over the relatively negligible amount liberated at lower temperatures, and distinct indications of slow but measurable decomposition. The moisture obtained here hardly indicates decomposition, but this is a less sensitive indicator than the gas. Incidentally it might be added that we have been able to take coals and organic materials such as starch and cellulose to higher temperatures without decomposition, and from experience with such substances we concluded that our graphitic acid still retained measurable amounts of water as such, after heating at 184° C.

We were evidently dealing with an exothermic compound, and the explosion was assumed to be due to the inability of the heat to dissipate rapidly enough when the rate of decomposition became considerable.

Our next attempt was to determine the vapor pressure of this graphitic acid on removing successive amounts of water. The apparatus used is shown diagrammatically in Figs. 1 and 2. After the sample had been weighed into tube *A* and the closed tube *B* was inserted to take up dead space, solid CO_2 was filled into the Dewar flask so as to retain the moisture in the condenser tube *E*. In order to avoid loss of moisture while removing air from the system, the end of tube *A* was placed in ice water, and the system evacuated with a Topler pump. (Fig. 1.) Stopcock *S* was now closed and the tube *A*, containing the sample, brought to the chosen constant temperature and the vapor pressure read. (A scale was fastened to the manometer and the pressure read on this scale by means of a telescope from a distance. It was possible to get readings to 0.01 mm.) The condenser tube *E* was now cut out and the moisture determined by weighing. We have proven (*l. c.*) that all of the moisture is removed from the gases which pass through this condenser and that the determinations are very exact. The condenser was now sealed in place, evacuated and the cock *S* opened for a time to allow some moisture to distill over from the graphitic acid to the condenser *E*. If any gas was present or evolved it was collected by the Topler pump. The fall tube *L* was calibrated so that we were able to measure even traces of gas with precision.

By repeating this process we obtained a series of vapor pressures corresponding to the different amounts of water removed. The observations made are given in the tables below:

TABLE I. *Sample A (b). Temperature 25° C.*

Percent Water Removed	Vapor Pressure
0.97	5.00 mm.
2.43	3.54 "
4.36	2.00 "
6.59	1.21 "
7.84	0.85 "
8.52	0.54 "
9.93	0.36 "
10.31	0.30 "
12.68	0.12 "

Our second experiment was performed at 56.5° C. (boiling point of acetone) with the following results:

TABLE II. *Graphitic Acid A (a). Temperature 56.5° C.*

Percent Water Removed	Vapor Pressure
5.98	6.25 mm.
9.71	18.35 "
10.88	7.88 "
11.68	4.48 "
12.09	3.40 "
12.66	2.40 "
13.48	1.54 "
13.88	1.20 "

These results are also represented graphically in Figs. 3 and 4.

It is to be observed that the vapor pressure continually decreases upon the removal of water, and there was no indications that these curves would not have continued without breaks had the experiment been carried further. But the rate at which the water was distilling from the graphitic acid had become so slow that the observations were discontinued.

If graphitic acid is a compound of the composition indicated by the formulas given by different investigators, and in addition contains water, for the substance is hygroscopic, then on removing this water we would expect a break in the curve at the point at which all the extraneous water disappears. But there is decidedly nothing of the kind to be observed in the results we have obtained. Our graphitic acid was air dried, and could be handled without gain or loss of moisture. Combustion averages showed the following:

Sample A (a)	Sample A (b)
C 50.74	C 51.34
H_2 2.65	H_2 2.55
Ash 1.60	Ash 2.48
O_2 44.91	O_2 43.63

If we assume that all the hydrogen is present as H_2O there would be 23.85 percent water (determined as above, 23.30) in *A*

(a) and 22.95 (determined 22.90) in *A* (b). At 25° C. we removed 13.88 percent, leaving 9.97 percent in *A* (a), and in the case of *A* (b) 13.1 percent, leaving 9.8 percent. If we consider the formulas that have been suggested by the various investigators and calculate the hydrogen to water, the percentage will be as given in Table IV.

TABLE IV.

Investigator	Formula	Percent of H_2O Calculated from the Hydrogen	Atomic Ratio, 100 Carbon to *x* Oxygen, After Deducting Water *x*
Brodie	$C_{11}H_4O_5$	16.7	27.3
Gottschalk	$C_{11}H_4O_6$	15.50	36.3
Luci	$C_{28}H_8O_{12}$	16.04	31.2
Berthelot and Petit	$C_{28}H_{10}O_{13}$	15.36	35.7
" " "	$C_{13}H_4O_7$	13.30	38.4

We have passed through all these percentages without a suggestion of a break, so that it is to be concluded that these formulas have no significance.

It is to be noted that the atomic ratio (column 4) of carbon to oxygen varies considerably. These represent the earlier results before the analytical methods had been perfected. Graphitic acid is a very difficult substance to handle due to its explosibility and hygroscopicity. The ash which varies from 0.5 to 2.5 percent has been a difficult factor to determine. Furthermore it has developed that considerable attention must be given to the complete conversion of graphite to graphitic acid. The Bureau of Mines work has shown that products which to all appearances were entirely graphitic acid showed, on careful microscopic examination, traces of unconverted graphite.

Balbiano (*l. c.*) decomposed his products by heat, analyzing the gases for CO, CO_2 and H_2O, then analyzing the non-explosive residue. We have here a large number of determinations made on graphitic acids from three different kinds of graphite and by two methods. The later results by Kohlschütter and Haenni and Selvig and Ratliff are also included in Table V as of equal reliability. We have eliminated the hydrogen as water and calculated the atomic ratio of carbon to oxygen.

TABLE V.

	C	H_2	O_2	For 100 Atoms of Carbon x Atoms Oxygen (H eliminated as water) x
		Balbiano's Results.		
(Brodie Method)				
Pinerole	57.60	1.52	40.97	37.5
Ceylon	56.51	1.75	41.74	36.8
(Staudenmaier Method)				
Pinerole	59.15	1.42	39.41	36.6
	58.43	1.66	39.91	33.7
Ceylon	59.09	1.42	39.49	35.6
	57.30	1.62	40.58	36.2
Acheson	59.35	1.42	39.33	35.5
	58.45	1.43	40.07	38.5
				or 36.4
		Kohlschütter and Haenni's Results.		
	59.02	1.91	39.07	30.3
	56.40	2.11	41.49	32.7
	55.30	2.26	42.44	32.9
	54.70	2.01	43.30	37.3
	54.40	2.14	43.46	36.3
		Selvig and Ratliff's Results.		
Ceylon	50.74	2.65	44.91	35.1
	50.49	2.63	47.36	35.6
Acheson	54.69	2.44	42.87	31.6
Dehydrated in vacuum	57.57	1.27	36.83	34.8

The oxygen is always determined as the residual difference, and so contains all the errors of the determinations of C, H_2 and ash. In view of this fact we may consider the results obtained by the later investigators as quite satisfactory, although they leave some uncertainty as to the exact ratio of carbon to oxygen in graphitic acid. If there is a compound such as C_2O the atomic ratio would be $C_{100}O_{33\cdot3}$, which is somewhat lower than indicated by

the results given above. $C_{11}O_4$ would show a ratio of $C_{100}O_{36.3}$, which seems to be very close to the best data we have.

Our results point clearly to the assumption that graphitic acid is a colloidal oxide of carbon, and when we consider the microscopic evidence, that the graphitic acid flakes are made up of exceedingly small plates of ultra-microscopic thinness, we can readily understand the situation, for it would seem that the total surface area of a gram of this substance is much larger than ordinary colloidal matter, and the amount of moisture on these surfaces and between the thin plates may readily be as great as represented by the hydrogen content of the most thoroughly dehydrated products. We have in vacuum readily removed moisture down to 10 percent, assuming that all the hydrogen is present as water.

If the graphitic acid flakes are 2 $\mu\mu$, or 20 molecules, thick, it would be possible to accommodate 10 percent of water in a layer only one molecule deep, and under such conditions it is doubtful if we could remove any of this water by ordinary drying agents. We have found that when the moisture is reduced to 10 percent the vapor pressure of the substance is only about 0.10 mm. The microscopic evidence indicates that the plates are probably less than 6 $\mu\mu$, thick, so that our assumptions are well within the evidence at hand.

Brodie found that graphitic acid would readily take up barium when shaken with a solution of $Ba(OH)_2$, and gave some analyses and formulas for the products formed. Berthelot and Petit found that more barium was taken up than indicated by Brodie, and Balbiano (*l. c.*) found that there was no definite limit. If we are dealing with a colloidal oxide of carbon, as we have assumed, these observations are quite explainable, also the difficulty encountered in completely oxidizing graphite by the Brodie method, and need of frequent washing. Furthermore, the colors, especially the green of the Staudenmaier method, are characteristic of colloidal substances. Different varieties of graphite would very probably give different average size of plates and so different amounts of adsorbed water, and in general different characteristics.

H. E. Armstrong (J. Soc. Chem. Ind. (1905), **24**, 475) concluded that ordinary oxides of carbon, CO and CO_2, resulted

from the breakdown of a complex oxide of carbon, and Read and Wheeler (J. Chem. Soc. (1912), **101**, 831; **103**, 461) have developed this idea more in detail. These authors consider that carbon is first oxidized to some compound C_xO_y which is a solid and decomposes into ordinary oxides of carbon. We have some work on the relation of oxygen to charcoal (soon to be published) which gives some excellent evidence in support of this viewpoint. We think that there may well be several oxides of carbon, solids at ordinary temperature, and some of them rich in carbon and poor in oxygen that are quite stable substances. The existence of such compounds as C_3O or $C_{11}O_4$ is quite probable.

SUMMARY.

We have investigated the relations of water to graphitic acid and have found that on removing water from this substance that the vapor pressure drops perfectly continuously without a suggestion of a break. The relation of water to graphitic acid is exactly that of moisture to a colloidal substance, which readily adsorbs water on large surfaces.

The translucent graphitic acid plates are made of an infinity of plates of excessive thinness. The relation of water to this substance and its variable properties are readily interpreted on the assumption that graphitic acid is a solid oxide of carbon with an exceptionally large surface covered with adsorbed water. The information available indicates formulas of the order C_3O or $C_{11}O_4$.

There is in the literature considerable evidence pointing to the existence of oxides of carbon, C_xO_y, rich in carbon and poor in oxygen.

Laboratory of Physical Chemistry,
Princeton University, March, 1920.

DISCUSSION.

F. A. J. FITZGERALD[1]: When I was working with the Acheson Graphite Company the question arose as to whether or not Acheson graphite electrodes were pure graphite or not, and we thought

[1] FitzGerald Laboratories, Inc., Niagara Falls, N. Y.

this might be determined by converting samples into graphitic acid or graphitic oxide. Much experimental work was done with the idea of determining the percentage of carbon present in the electrodes as graphite, but I finally abandoned the work, having come to the conclusion that I was not competent to work out a satisfactory method.

There is a reference in the paper to Staudenmaier's method. As I remember it this followed the treatment with potassium chlorate and nitric acid, the residue being treated with potassium permanganate followed by hydrogen peroxide. This method apparently saved much time diminishing the number of treatments with the nitric acid mixture. Did the author of this paper use the method?

When graphite oxide is heated it decomposes explosively leaving a black residue called by Brodie pyro-graphitic oxide. Did Mr. Hulett make any study of this material? Is it carbon or a compound of carbon?

In my work with graphitic oxide the most satisfactory graphite for the purpose was made from a coal obtained from the Skenhana vein of the Castelcomer mines in Ireland. The graphite from this coal was different from any other anthracite-coal graphite I ever saw. We got several tons of this coal for graphitizing and we found it had a very remarkable property. The furnace in which it was graphitized was built in the usual way, that is, as a trough containing the crushed coal through which the current was passed. When the coal graphitized it expanded enormously, pushing out the walls of the furnace. The graphite from this coal also shows the swelling phenomenon in a very marked degree when treated with HNO_3 and then heated.

E. O. BENJAMIN[2]: About six months ago the subject in connection with graphite was brought to my attention by Mr. Kirk Brown. He stated that Mr. Aylesworth, who is the inventor of Condensite, produced a form of graphite which had about seven times the volume of any known form of graphite up to date.

Mr. Aylesworth is dead now, and apparently the process by which he arrived at the method of producing this form of graphite has died with him. However, a bottle containing a sample is kept at the plant of the Condensite Company of America in Bloomfield,

[2] International Oxygen Co., Newark, N J.

and I believe if anyone will see Mr. Brown, who is the manager of that company, he could obtain a small amount of this so that it would be possible to arrive at this solution of how this form of graphite can possibly be reproduced. Its microscopic appearance seems to be something like that of a book turned over on its back and the leaves opened up fan-shape, presenting an enormous surface of small scales.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

THE PROBLEM OF DETERMINING GRAPHITIC CARBON.[1]

By W. A. Selvig[2] and W. C. Ratliff.[3]

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[1] Published by permission of the Director, U. S. Bureau of Mines. Manuscript received March 16, 1920.

[2] and [3] Bureau of Mines, Pittsburgh, Pa.

INTRODUCTION.

Purpose of Investigation.

The experiments described in this paper were undertaken in the course of investigations on graphite by the Bureau of Mines. The chemists of the Bureau were asked to determine the percent of graphitic carbon in certain graphite-like mineral deposits and coke. These materials were calcined commercially for the manufacture of carbon electrodes and samples were sent to our chemical laboratory for the determination of the degree of graphitization. So far as the authors have been able to ascertain, no direct quantitative method for the determination of graphitic carbon in the presence of amorphous carbon has been developed.

HISTORICAL REVIEW.

B. C. Brodie, 1859.

When Brodie[4] sought to ascertain the weight with which carbon in the form of graphite entered into combination, he discovered a new substance. Upon treating Ceylon graphite with a mixture of potassium chlorate and fuming nitric acid he found that it increased in weight and when subjected to heat disintegrated with violent evolution of gas, leaving a black fluffy carbonaceous substance. By repeated treatments of the graphite with the oxidizing mixture he isolated this new substance in the form of minute brilliant and translucent plates, light yellow in color and insoluble in all solvents. He attempted to assign to this substance a definite crystalline structure, and named it graphitic acid. Upon analysis he assigned to it the formula $C_{11}H_4O_5$. When the solid was shaken up with barium hydrate, Brodie found that it took up barium, forming two products, to which after analysis, he assigned the formulæ $C_{11}H_3BaO_5$ and $C_{22}H_7BaO_{10}$.

M. Berthelot, 1870.

M. Berthelot[5] studied this substance more extensively. He observed the action of the Brodie mixture upon different varieties of amorphous carbon and graphites. The amorphous carbon was converted to humic acids, giving a yellowish-brown solution in

[4] Brodie, B. C., On the atomic weight of graphite: Philosophical Transactions of the Royal Society of London (1859), 149, (1), 249-259.

[5] Berthelot, M., Recherches sur les États du Carbone: Annales de Chimie et de Physique (1870), 259, [4], 19, 392-427.

water, while the graphites gave the insoluble graphitic oxides, as he styled them. He treated natural graphites, graphite from foundry iron and graphite obtained by the transformation of different varieties of carbon under the influence of the electric arc, and obtained from each of these graphites graphitic oxides of slightly different properties.

L. Staudenmaier, 1898 and 1899.

The work of L. Staudenmaier[6] on graphitic acid is somewhat different from any of the earlier investigators. He prepared it by treating Ceylon graphite with concentrated sulphuric and nitric acids and then adding slowly, with stirring, potassium chlorate. This changed the graphite to a green product which on washing and subsequent treatment with a mixture of potassium permanganate and sulphuric acid gave a yellow insoluble graphitic acid very similar to that of Brodie.

M. Georges Charpy, 1909.

Charpy[7] studied the action of various oxidizing mixtures on different forms of amorphous carbon and graphites. He found that a mixture of concentrated sulphuric acid and potassium permanganate slowly converted graphite to graphitic oxide at ordinary temperatures, but if heated to approximately 100° C. the reaction was very rapid, part of the carbon passing off as carbon dioxide.

A mixture of sulphuric and chromic acids acted similarly to the permanganate mixture, but under like conditions liberated carbon as carbon dioxide much more rapidly. At ordinary temperatures, if the reaction was stopped in time it was found that graphitic oxide was formed, which by prolonged treatment with the oxidizing mixture was, however, converted to carbon gases. He found that by treating graphitic carbon at ordinary temperatures with the Brodie mixture the carbon was gasified very slowly, but that if the temperature was raised this reaction was more rapid. Charpy obtained the figure of 2.25 as the density of graphite.

[6] Staudenmaier, L., Verfahren zur Darstellung der Graphitsäure: Berichte der Deutschen Chemischen Gesellschaft (1898), 31, (2), 1481-1487; (1899), 32, (2), 1394-1399.

[7] Charpy, M. Georges, Sur la formation de l'oxide graphitique et la definition du graphite: Comptes Rendus der Séances de L'Académie des Sciences (1909), 148, 920-923

M. L. Balbiano, 1916.

Balbiano[8] made quite an extensive study of graphitic acid. He prepared it from Ceylon, Pinerole and Acheson graphites, and upon analysis figured that its composition could be represented by the two limiting formulæ, $C_{13}H_4O_7$ and $C_{14}H_4O_7$. He concluded that graphitic products which have in common the property of deflagrating when heated rapidly and which differ in color according to the original graphite and method of preparation, are nothing but absorption products of graphite, water, carbon monoxide, and carbon dioxide, whose composition varies within narrow limits.

Von V. Kohlschütter and P. Haenni, 1918.

Kohlschütter and Haenni[9] made a study of the action of oxidizing mixtures on graphite and the behavior of graphitic acid. As nitric acid possesses the property of penetrating between the plates of the graphite flake, they concluded that in oxidizing mixtures nitric acid served as a carrier in introducing the oxidizing mixture into the graphite flake. In oxidizing mixtures consisting of HNO_3, H_2SO_4 and $KClO_3$, they concluded that ClO_2 was the active oxidizing reagent and that the nitric acid assisted in introducing it into the graphite flake.

METHODS FOR THE ESTIMATION OF GRAPHITIC CARBON.

Specific Gravity Test.

Arsem[10] defines graphite as that allotropic form of carbon having a specific gravity of 2.25 to 2.26. He determined the specific gravity of the pulverized samples in a pyknometer by boiling with C.P. benzene.

Electrical Conductivity Test.

An empirical method for the estimation of the degree of graphitization of material used for making electrodes has been used. The method consists in measuring the electrical conduc-

[8] Balbiano, M. L., Etude sur l'acide graphitique: Bulletin de la Societe Chimique de France (1916), **109**, [4]; **19**, (1), 191-203.

[9] Kohlschütter, Von V., and Haenni, P., Zur Kenntnis des graphitischen Kohlenstoffs und der Graphitsäure: Zeitschrift für anorganische und allgemeine Chemie (1919), **105**, 121-144.

[10] Arsem, W. C., Transformation of other forms of carbon into graphite; Trans. Am. Electrochemical Soc. (1911), **20**, 105-119.

tivity of the powdered material, which is packed in porcelain-lined metal tubes and subjected to a known pressure.

EXPERIMENTAL WORK.

Action of Oxidizing Mixtures on Amorphous Carbon.

One of the first problems was to determine whether or not amorphous carbon could be completely removed by treatment with oxidizing mixtures. One-half gram samples of bituminous coal, anthracite coal, and coke, ground to 60 mesh, were treated by the Brodie[12] method, using 10 cc. of fuming nitric acid (sp. gr. 1.5) and 4 grams of powdered potassium chlorate per half-gram of sample. The samples were added to the fuming nitric acid and the chlorate added in small portions with constant stirring; after violent reaction had ceased the whole was placed in a water bath, the temperature raised to 60° C. and held at this point for 10 to 12 hours. Then the mixture was diluted with water to about 300 cc., thoroughly stirred and allowed to settle, after which the clear reddish-brown solution of humic acids formed by the oxidation of the amorphous carbon was syphoned off. The washings were repeated until the syphoned liquid was no longer colored and the residue then dried on the steam bath and again treated with the oxiding mixture. The samples were given a third treatment. The coal samples showed no trace of a brown color in the first wash water, indicating the removal of all amorphous carbon possible by the first two treatments, while the coke gave a colored wash water. Five treatments in all were required for the complete removal of amorphous carbon from the coke, as evidenced by the absence of color in the first wash water after the sixth treatment.

The Staudenmaier[13] method was also tried on the coal and coke samples. One-half gram samples were treated with the following oxidizing mixture: 14 cc. of concentrated sulphuric acid (sp. gr. 1.84), 6 cc. of concentrated nitric acid (sp. gr. 1.42), and 18 grams of powdered potassium chlorate. The acids were thoroughly mixed with the sample and the chlorate added slowly with constant stirring, but the mixture exploded violently before all

[12] Brodie, B. C., On the Atomic Weight of Graphite: Philosophical Transactions of the Royal Society of London (1859), 149, (1), 249-259.

[13] Staudenmaier, L., Verfahren zur Darstellung der Graphitsäure. Berichte der Deutschen Chemischen Gesellschaft (1899), 32, (2), 1394-1399.

of the chlorate was added. Repeated attempts were made to add all of the chlorate, but even in an ice-bath the mixture always exploded.

The residues from the treatment of the coal and coke samples by the Brodie process were burned in a combustion furnace to determine the amount of remaining carbon. Carbon was still present in the following percentages of the original carbon:

Material	Percent of Original Carbon in Residue
Bituminous coal	1.01
Anthracite coal	0.81
Coke	0.75

The residue from the coke samples showed a slight deflagration when heated suddenly, indicating the presence of graphitic acid. This test would indicate the presence of some graphitic carbon in coke. The residues from the coals gave no deflagration upon heating, indicating the absence of graphitic acid. It is very probable that further treatment of the coal samples with the oxidizing mixture would have removed the small amount of carbon remaining in the residue.

Action of Oxidizing Mixtures on Graphitic Carbon.

When graphite is subjected to certain oxidizing mixtures, such as the Brodie or Staudenmaier, under certain conditions the graphitic carbon is converted principally to graphitic acid of varying shades of yellow, the color varying largely with the kind of graphite used. The ease with which the oxidizing mixtures attack the different varieties of graphite depends largely upon the fineness and structure of the graphite.

The Acheson graphite used in the tests was finely powdered and was very readily converted into graphitic acid by both the Brodie and Staudenmaier methods. When subjected to the Staudenmaier reaction it was necessary to keep the mixture at a low temperature, about 0° C., while the $KClO_3$ was added, otherwise the reaction proceeds with explosive violence.

Preparation of Graphitic Acid.

Graphitic acid was first prepared by us from Ceylon graphite by the Brodie method, using 10 cc. of fuming nitric acid and 4 grams of powdered potassium chlorate per 0.5 gm. of graphite.

The graphite was stirred into the acid and the chlorate added to the mixture in small portions with constant stirring. When thoroughly mixed the whole was placed in a water bath, the temperature raised to 60° C. and held at this point for 10 to 12 hours. The resulting green oxidation product was mixed with about 400 cc. of water and allowed to settle. After syphoning off the clear liquid the residue was dried on the steam bath and given a second treatment with the oxidizing mixture. In all, five such treatments were necessary to complete the oxidation of the graphite and produce graphitic acid of a bright yellow color.

Ceylon graphite was also treated with three times its weight of powdered potassium chlorate and enough fuming nitric acid to make a thin paste, and heated on the steam bath for three days. When washed it showed only a green oxidation product with no trace of yellow, substantiating Brodie's experience that the yellow substance cannot be produced by one prolonged treatment.

Samples of Ceylon graphite were next treated according to the Staudenmaier method, using 28 cc. of concentrated sulphuric acid (sp. gr. 1.84), 12 cc. of concentrated nitric acid (sp. gr. 1.42), and 36 grams of potassium chlorate per gram of graphite. This reaction is more violent than the Brodie reaction and care must be exercised to control it.

The graphite was stirred into the mixture of the acids and the whole placed in an ice bath. The potassium chlorate was added in small portions with constant stirring, the time for the addition of the 36 grams being approximately 30 minutes. It is necessary that the temperature be kept very low during the addition of the chlorate, to prevent explosions. After allowing the mixture to remain in the ice bath for about 2 hours, it was set aside and kept at room temperature for about 24 hours, then washed with water to remove any excess acids and soluble material and treated with potassium permanganate and sulphuric acid; 7 grams of permanganate to 120 cc. of 1/3 sulphuric acid. After heating on the steam bath for about 30 minutes the excess permanganate and oxides of manganese formed during the reaction were destroyed by the addition of hydrogen peroxide. When washed and dried on the steam bath the material was black, showing no signs of either a green or yellow color, but deflagrated readily when heated over a free flame. Mixtures were allowed to stand for longer

periods of time before treating with the permanganate and sulphuric acid and it was found that about six days were necessary to produce graphitic acid of a bright yellow color from Ceylon graphite.

For further study of the acid, a large quantity was prepared by treating 40 grams of Ceylon graphite according to the Brodie method, using 500 cc. of fuming nitric acid and 200 grams of potassium chlorate per treatment. After the third treatment the oxidation product was still green. A small portion of it was treated with potassium permanganate and sulphuric acid as in the Staudenmaier process, which produced graphitic acid of a bright yellow color, with seemingly no traces of unoxidized material. The entire amount was treated in this manner, giving a large quantity of bright yellow graphitic acid.

An equal amount of Acheson graphite was also treated in a similar manner and after the first treatment with the oxidizing mixture it was found that the resulting green product when treated with sulphuric acid and potassium permanganate was readily converted to yellow graphitic acid.

The particles of Ceylon graphite ranged in size from approximately 20 to 80 mesh, while the Acheson was a very fine powder, which seems to indicate that in the case of graphites the fineness of the material is one of the factors in the rate of oxidation; also that the oxidation is greatly hastened by supplementing the Brodie method with the sulphuric acid and potassium permanganate treatment. It will be understood that this modification of the Brodie method was employed on all of the remaining graphite samples treated in these experiments by the Brodie method.

Drying of Graphitic Acid.

Experiments were made to determine the most satisfactory conditions for drying the graphitic acid preparatory to analysis. One gram samples of the graphitic acid from Ceylon graphite were weighed out on 3-inch watch-glasses and placed in desiccators over concentrated sulphuric acid. Drying was carried on both at normal and reduced pressure. The time of drying, in hours, and the percent loss in weight are given in Table I.

There seems to be no point at which the weight of the graphitic acid remains constant, as the drying for different lengths of time

TABLE I.

Time of Drying and Percent Loss in Weight of Graphitic Acid from Ceylon Graphite at Normal and Reduced Pressures.

Normal Pressure			Diminished Pressure (40 mm.)				
				Sample No. 1		Sample No. 2	
Time Hours	Weight of 1 Gram Sample	Percent Loss	Time Hours	Weight of 1 Gram Sample	Percent Loss	Weight of 1 Gram Sample	Percent Loss
..	1.0000	....	..	1.0000	....	1.0000	....
24	0.9039	9.61	24	0.7941	20.59	0.7955	20.45
72	0.8933	10.67	70	07879	21.21	0.7807	21.93
79	0.8943	10.57	77	0.7946	20.54	0.7876	21.24
96	0.8926	10.74	94	0.7916	20.84	0.7845	21.55
102	0.8940	10.60	100	0.7917	20.83	0.7846	21.54
120	0.8931	10.69	118	0.7902	20.98	0.7835	21.65
127	0.8942	10.58	125	0.7931	20.69	0.7869	21.31
144	0.8928	10.72	143	0.7911	20.89	0.7836	21.64
174	0.8911	10.89	172	0.7883	21.17	0.7821	21.79
606	0.8868	11.32	..	....	....	....	....
654	0.8876	11.24	..	....	....	....	....
962	0.8879	11.21	..	....	....	....	....

TABLE II.

Moisture Changes in Graphitic Acid From Ceylon Graphite when Exposed to Air of Laboratory, at Laboratory Temperatures.

Time Days	Weight in Grams	
	Sample No. 1	Sample No. 2
..	0.8957	0.7258
1	0.8813	0.7114
2	0.8963	0.7311
3	0.9242	0.7488
4	0.9353	0.7541
5	0.9138	0.7393
6	0.9305	.....

gave varying amounts of loss in weight. Although the samples were weighed in air, the weighings were made as rapidly as possible. The graphitic acid is evidently very susceptible to changes in humidity. Samples of the same graphitic acid were allowed to air-dry for a period extending over 6 days, weighings being made at 24-hour intervals. The results of this test are given in Table

II. The weight of the graphitic acid is seen to vary considerably and it evidently takes up or loses moisture readily with varying humidity changes of the surrounding air.

The fluctuations in weight are no doubt due to changes in moisture content, since it has been shown by Dr. G. A. Hulett that practically no carbon gases come off below 180° C. The above table clearly shows that the graphitic acid does not remain constant in weight, and that special precautions must be taken in weighing portions for analysis.

Since it was necessary during some of these experiments to determine the weight of carbon contained in a sample of graphitic acid made from a weighed quantity of graphite, a method had to be employed in weighing out the sample for analysis whereby these fluctuations in weight due to a changing moisture content would be eliminated. The entire sample of graphitic acid was weighed and immediately the portions for analysis weighed out.

Analysis of Graphitic Acid.

As practically all of the amorphous carbon can be removed from carbonaceous materials, such as coal and coke, by the Brodie method, and having obtained large samples of graphitic acid from both natural and artificial graphites, the next step was to analyze the graphitic acid with special reference to the carbon content. The ease with which it deflagrates with rapid evolution of gases when heated to about 200° C. makes the analysis a difficult one. Balbiano[14] made the analysis in two stages. He heated a weighed quantity of the acid in vacuum, collected the gases given off and determined the amount of carbon present. After gases ceased to be rapidly evolved, there remained a black residue which could be burned without deflagration. This gave him the total amount of carbon. But this is tedious and not as accurate as direct combustion. By careful manipulation the analysis can be made in one step. An electrically heated combustion furnace[15] was used, the absorption train consisting of a Marchand tube filled with granular calcium chloride for absorbing moisture, to which was connected a Vanier potash bulb containing a 30 percent potassium hydroxide solution for absorbing the carbon dioxide.

[14] Balbiano, M. L., Etude sur l'acide Graphitique: Bulletin de la Societé Chimique de France (1916), 109, [4]; 19, (1), 191-203.

[15] Stanton, F. M., and Fieldner, A. C., Methods of Analyzing Coal and Coke: Technical Paper 8, Bureau of Mines, 1913. 22-24.

When graphitic acid burns the reaction is exothermic, but when it is intimately mixed with some non-combustible material which separates the particles and takes care of the heat evolved so that the reaction rate does not get beyond control, it was found that the substance could be easily burned without deflagration.

A one-tenth gram sample of graphitic acid was weighed into a porcelain combustion boat about 10 cm. long and 1 cm. wide, thoroughly mixed with previously ignited finely divided copper oxide, and this mixture covered with a fairly thick layer of copper oxide. The temperature was held at about 100° C. for the first 15 minutes of heating, then it was slowly increased for some 30 minutes until a faint glow was observed. From here it was increased rather rapidly to a good red heat, approximately 800° C., requiring some 15 minutes. During this first hour of burning a slow current of dry purified air was aspirated through the apparatus to sweep out the products of combustion. To insure complete combustion the current of air was replaced with purified oxygen for about 10 minutes, followed by an air current for about 15 minutes. Then the absorption bulbs were removed, allowed to come to room temperature and weighed. This affords a very accurate and easily controlled method for determining the carbon and hydrogen content of graphitic acid, all in one direct process.

Analyses of Natural and Artificial Graphites.

In all, four graphites were used in these experiments. Of the natural graphites, Ceylon, Alabama and Pennsylvania were used, while the finely powdered Acheson represented the artificial class. The analyses of these graphites is given in Table III.

TABLE III.

Analyses of Natural and Artificial Graphites.

Graphite	Moisture Percent	Volatile Matter Percent	Ash Percent	Determined by Direct Combustion		Determined by Combustion After Special Treatment	
				Carbon Percent	Hyro-gen Percent	Carbon Percent	Hydro-gen Percent
1	2	3	4	5	6	7	8
Ceylon	0.06	0.82	4.15	95.91	0.18	95.58	0.14
Pennsylvania...	0.01	1.26	9.65	90.05	0.34	89.74	0.15
Alabama	0.08	1.20	8.80	90.75	0.18	90.17	0.21
Acheson	0.10	0.56	0.10	99.38	0.06	98.89	0.06

the humus matter having been removed by the second treatment as evidenced by the absence of any color in the wash-water after the third treatment. But such was not the case with the graphite-coke mixtures. Five treatments were necessary to remove all of the amorphous carbon, as shown by the absence of color in the wash-water of the sixth treatment. At this point the samples presented the same green color as the others.

As stated earlier in the paper, under "preparation of graphitic acid," the oxidation of the graphite after it has reached this characteristic green stage can be greatly facilitated by treating with sulphuric acid and potassium permanganate. So, in order to save time all of the samples were given this treatment at this point. Approximately 150 cc. of 1/3 sulphuric acid was added to each sample and about 1 gram of potassium permanganate stirred in. They were heated on the steam bath for about 30 minutes and then hydrogen peroxide was added with thorough agitation until all excess permanganate and any precipitated oxides of manganese were destroyed. The graphitic acid formed in each case was yellow, but of slightly different shades. That from the Acheson graphite was the brighest yellow in color; that from Ceylon slightly darker, while that from Pennsylvania and Alabama was darker still, more of an orange than yellow.

At this point the oxidation appeared to be complete. The samples were thoroughly washed by decantation through tared Gooch crucibles, using filter paper pads of one thickness only, the bulk of the sample remaining in the beaker until washing was practically complete. The samples were washed with distilled water until the washings no longer showed acid to litmus. Then for the final washings alcohol and ether were used to remove as much of the water as possible, and the samples allowed to air dry.

The treatment of the graphite samples by the Staudenmaier process was carried out as follows: The 0.5 gm. sample of graphite was stirred into a mixture of 14 cc. of concentrated sulphuric acid (sp. gr. 1.84) and 6 cc. of concentrated nitric acid (sp. gr. 1.42) and placed in an ice bath. The potassium chlorate, 18 gm. in all, was added in small portions with constant stirring, the time necessary for adding the entire amount being about 30 minutes. The mixture was allowed to remain in the ice bath for about thirty minutes after all the chlorate had been added, and

was frequently stirred. After violent reaction had ceased the mixture was removed from the ice bath and allowed to stand at room temperature for six days with occasional stirring. At the end of this time a large volume of water, about a liter, was added, and after very thorough stirring, allowed to settle over night and the clear liquid syphoned off. If no traces of excess chlorate or any salt formed during the reaction are noticeable, the sample is ready for the final oxidation with potassium permanganate and sulphuric acid. Some of the samples treated in these experiments required a second washing. The washed material was of a darker green color than the green oxidation product produced by the Brodie method. After being thoroughly washed, the samples were treated with potassium permanganate and sulphuric acid for the final oxidation, in the same manner as described above in the Brodie treatment. In fact the treatment from this point on, washing, etc., was identical with that of the Brodie treatment.

As previously stated, graphitic acid is very susceptible to moisture changes, so the above samples were prepared for analysis as explained under "drying of graphitic acid." The entire sample was weighed immediately before weighing out the samples for the carbon and hydrogen determinations. Four 0.1 gm. samples were weighed out for analysis, two being for reserve in case a second determination was necessary. These samples were burned in the electric resistance combustion furnace for carbon and hydrogen content, as explained under "analysis of graphitic acid." After obtaining the percent of carbon in the graphitic acid and the exact weight of the entire sample at the time, the sample for analysis was taken, the weight of the total amount of carbon in the sample was calculated; and since the entire sample of graphitic acid was obtained from a known weight of graphite the percent of graphitic carbon in the original graphite sample was readily calculated. This was checked against the percent of graphitic carbon in the same graphite, as previously determined by direct combustion. The results of these analyses are given in Tables IV, V and VI.

Discussion of Results. Table IV gives a comparison of the graphitic carbon content of each of the graphites, as determined by the following methods:

(1) By converting a weighed amount of each graphite to graphitic acid by both the Brodie and Staudenmaier methods, determining the carbon content of the graphitic acid by direct combustion to CO_2, and thus calculating the percent of graphitic carbon in the original graphite sample.

(2) By direct combustion of the different graphites to CO_2.

TABLE IV.

Percent Carbon as Determined by Direct Combustion of Graphites and by Combustion of Graphitic Acid Obtained from the Graphites.

Kind and Specific Gravity* of Graphite	Percent Carbon						Percent Carbon in Graphites by Direct Combustion	Difference in Determined Carbon	
	Conversion to Graphitic Acid by Brodie Method			Conversion to Graphitic Acid by Staudenmaier Method					
	Sample A	Sample B	Average	Sample A	Sample B	Average		Columns 4 & 8	Columns 7 & 8
1	2	3	4	5	6	7	8	9	10
Ceylon graphite, sp. gr. 2.27..	94.2 94.1	92.8 92.4	93.4	95.2 94.8	94.5	94.8	95.9	2.5	1.1
Alabama graphite, sp. gr. 2.30..	74.9 75.0	76.0 76.0	75.5	78.3 78.5	77.7 77.3	78.0	90.8	15.3	12.8
Penna. graphite, sp. gr. 2.31..	71.6 71.3	69.3 69.0	70.3	72.4 72.0	. . .	72.2	90.0	19.7	17.8
Acheson graphite, sp. gr. 2.23..	94.1 93.8	93.3 93.3	93.6	96.3 95.7	95.7 95.6	95.8	99.4	5.8	3.6

* Specific gravity of graphites determined in a pyknometer by boiling with distilled water under reduced pressure.

Column 4 of Table IV gives the graphitic carbon content of each of the four graphites as determined by conversion to graphitic acid by the Brodie method; column 7 of the same table, by the Staudenmaier method. Column 8 gives the percent of graphitic carbon in each of the graphites as determined by direct combustion. The difference in the graphitic carbon content of the graphites as determined by conversion to graphitic acid and by

direct combustion is given in columns 9 and 10. It is noted that the difference is the least in the case of Ceylon graphite. The Acheson shows a slightly greater difference, while in the Alabama and Pennsylvania kinds the difference is decidedly pronounced.

TABLE V.

Percent Carbon as Determined by Direct Combustion of Graphites and by Combustion of Graphitic Acid Obtained from Treating Known Mixtures of Graphites and Amorphous Carbon by the Brodie Method.

Kind and Amounts of Material Used in Mixtures	Percent Carbon				Difference in Carbon Content as Given in Columns 4 and 5
	Conversion to Graphitic Acid by Brodie Method			Direct Combustion of Graphite	
	Sample A	Sample B	Average		
1	2	3	4	5	6
Ceylon graphite and coke. 0.5 g. each.....	94.0 93.5	95.8 95.9	94.8	95.9	1.1
Ceylon graphite and anthracite coal. 0.5 g. each.....	92.9 92.4	94.3 94.3	93.5	95.9	2.4
Ceylon graphite and bituminous coal. 0.5 g. each.....	93.3 93.4	93.4 93.7	93.4	95.9	2.4
Acheson graphite and coke. 0.5 g. each.....	93.5 93.8	92.1 91.7	92.8	99.4	6.6
Acheson graphite and anthracite coal. 0.5 g. each.....	97.1 97.5	95.7 95.2	96.4	99.4	2.8
Acheson graphite and bituminous coal. 0.5 g. each.....	96.1 95.8	. . . . . .	96.0	99.4	3.4

In all of these graphites the carbon as determined by conversion to graphitic acid and combustion of the same is less than the carbon determined by direct combustion of the graphites.

Table V gives the percent of carbon obtained by treating mixtures of graphites and amorphous carbon by the Brodie method

and the subsequent combustion of the graphitic acid obtained. Ceylon and Acheson graphites were used in making these mixtures, the amorphous carbon being in the form of anthracite and bituminous coal and coke. As the Brodie method of treatment removes the amorphous carbon, the results obtained in the above mixtures should be practically the same as results obtained on

TABLE VI.

Analyses of Air-Dried Graphitic Acid Obtained from Natural and Artificial Graphites by Brodie and Staudenmaier Methods.

Kind of Graphite	Method of Preparation. B—Brodie S—Staudenmaier	Percent		
		Carbon	Hydrogen	Oxygen Plus Ash by Difference*
Ceylon Graphite....	1—B.	50.60	2.95	46.45
	2—B.	52.60	2.55	44.85
	1—S.	51.22	2.81	45.97
	2—S.	52.44	2.50	45.06
Alabama Graphite..	1—B.	47.80	2.40	49.80
	2—B.	47.76	2.48	49.76
	1—S.	47.32	2.42	50.26
	2—S.	47.38	2.31	50.31
Pennsylvania Graphite..	1—B.	45.70	3.18	51.12
	2—B.	46.46	3.20	50.34
	1—S.	44.78	2.89	52.33
	2—S.	46.98	2.71	50.31
Acheson Graphite..	1—B.	52.99	2.52	44.49
	2—B.	46.84	3.04	50.12
	1—S.	50.40	2.65	46.95
	2—S.	50.22	2.63	47.15

* Ash content of graphitic acid from Ceylon graphite is about 2 percent. No ash determinations were made on graphitic acid from Alabama, Pennsylvania or Acheson graphite. The ash content of graphitic acid from Acheson graphite would be negligible, as the original graphite contained only 0.1 percent ash.

treating these graphite samples without any addition of amorphous carbon, which results are shown in Table IV. In the case of Ceylon graphite mixed with amorphous carbon, the percent of graphitic carbon obtained is practically the same as when the Ceylon graphite alone was treated with the oxidizing mixture. However, a larger variation is found in the results obtained by treating Acheson graphite alone and mixtures of Acheson graphite and amorphous carbon. The mixtures of Acheson graphite and

anthracite coal gave about three percent more graphitic carbon than the Acheson graphite alone. This difference was the greatest found. It is to be noted, however, that in duplicate samples with the same treatment differences of as high as 2.5 percent graphitic carbon were obtained, as shown in Tables IV and V. The presence of amorphous carbon in the samples, therefore, did not have any noticeable effect upon the results obtained.

The analyses by direct combustion of samples of graphitic acid obtained from the natural and artificial graphites by the Brodie and Staudenmaier methods are given in Table VI. These analyses were made on air-dried samples and give the data from which the results given in columns 2 to 7 of Table IV were calculated.

Ash determinations[16] were made on 0.2 gm. samples of graphitic acid obtained from Ceylon graphite by heating in a platinum crucible with 5 or 6 cc. of pure high-boiling petrolatum. The petrolatum takes care of the heat evolved during the first stages of heating when gases are rapidly given off from the graphitic acid. After this stage the temperature was raised gradually and the material burned to constant weight.

Referring to Table IV, columns 9 and 10, it is noted that in every case the percent of graphitic carbon, as determined by combustion of the graphitic acid obtained from the graphites, is lower than the carbon as determined by direct combustion of the graphites. These differences ranged from 2.5 percent in the Ceylon graphite to as much as 19.7 percent in the Pennsylvania graphite.

Examination under the microscope indicated one possibility of accounting for these large differences. Samples of the graphitic acid from the Alabama and Pennsylvania graphites showed upon examination quite a large amount of what appeared to be unoxidized graphite in the centers of the individual flakes. There was a possibility that the burning of the graphitic acid in the combustion furnace was not complete, due to the presence of considerable unoxidized graphite, since graphite is much more difficult to burn completely than graphitic acid. So, in addition to the regular time of burning, samples were burned in oxygen for periods of time ranging from 1 to 2½ hours with a change of potash bulbs

[16] Suggestions as to procedure of determining ash made by G. A. Hulett.

to determine whether combustion was actually complete, and they showed only a very slight increase in carbon content over that obtained by the usual period of burning.

But, in order to accurately check up this point, samples of the Alabama and Pennsylvania graphites were treated again in a similar manner and with control samples for determining when oxidation of the graphites to graphitic acid was complete. Small portions of these control samples were examined under the microscope after each treatment, and six treatments by the Brodie method and one with potassium permanganate and sulphuric acid were necessary for complete oxidation of the Alabama graphite to graphitic acid, while the Pennsylvania required eight of the Brodie and one of the permanganate and sulphuric acid. The Pennsylvania graphite, however, consisted of larger flakes, which perhaps accounted for the extra treatments.

The samples treated by the Staudenmaier method after standing for six days were not completely oxidized when given the permanganate-sulphuric acid treatment. These were washed, dried and again treated, this time standing four days before the permanganate-sulphuric acid treatment. Upon examination under the microscope, oxidation was found to be complete. Weighed portions of all the above samples were burned in the combustion furnace in the usual way, but gave practically the same results for the graphitic carbon content of the graphites as the samples given in Table IV. There was still another possibility that this large difference might be due to the evolution of carbon gases during the treatments.

Loss of Graphitic Carbon by Evolution as Carbon Gases.

An apparatus was set up for collecting the gases given off during the treatments. The Brodie method was employed, using a 0.5 gm. sample of Alabama graphite, containing 455.6 mg. (91.1 percent) carbon as determined by direct combustion to CO_2.

The apparatus consisted of the following parts arranged in the order named: (1) An air-purifying train, containing sulphuric acid and soda lime; (2) a reaction flask, containing the graphite and oxidizing mixture; (3) two gas washing bottles in series, containing saturated solutions of KI for removing chlorine and

oxides of chlorine and possibly oxides of nitrogen; (4) a 2½ liter evacuated bottle for collecting the sample of carbon gases. This bottle contained a small amount of mercury for removing any chlorine or oxides of nitrogen that might not be absorbed in the KI solution. The fuming nitric acid was added through a separatory funnel to the graphite-chlorate mixture in the flask and the collection of gases started at such a rate as would just prevent back pressure in the air train. The temperature was gradually raised to 60° C. and held at this point for 10 to 12 hours. During this time about 15 liters of gas was collected. The sample was given a second similar treatment and the gases from the two treatments analyzed for CO and CO_2. The results of this test are given in Table VII.

Table VII gives the analysis of the gases and shows that the major portion of the carbon gases is CO_2. Oxides of nitrogen were determined on some of the samples from the first treatment as they would be absorbed by the KOH and give a high CO_2 value, but they proved to be negligible. The fifth sample on the first treatment shows a large amount of CO_2, but at this point the temperature got up to about 90° C. This is in accordance with the statement by Charpy[17] that around 100° C. the evolution of carbon gases is rather rapid when natural graphite is treated with the oxidizing mixtures.

The first sample on the second treatment showed a large amount of CO_2; but this can perhaps be accounted for by the fact that during the washing and drying of the oxidation product after the first treatment, a considerable amount of CO_2 was occluded, and when treated with the oxidizing mixture the second time, it was rapidly evolved.

After the second treatment, the oxidation product was burned in a combustion furnace for the carbon content, and 82.0 percent of the carbon in the original sample was accounted for. This plus the 7.95 percent lost in the form of carbon gases makes a total of 90.0 percent, as compared to 91.1 percent carbon in the original sample. Since the graphite was given only two treatments, there would no doubt have been further evolution of carbon gases on further treatments.

[17] Charpy, M. Georges; Sur la formation de l'oxide graphitique et la definition du graphite, Comptes Rendus des Séances de L'Academie des Sciences (1909), 148, 920-923.

TABLE VII.

Composition of Gases Given Off During the Treatment of Alabama Graphite by the Brodie Method.

First Treatment

Bottle No.	Capacity cc.	Percent		Volume in cc.		Oxides of Nitrogen, Parts per Million
		CO_2	CO	CO_2	CO	
1	2560	0.15	0.02	3.84	0.51	6
2	2530	0.07	....	1.77	....	8
3	2530	0.07	....	1.77	....	..
4	2530	0.17	....	4.30	....	..
5	2570	0.85	....	21.85	....	90
6	2540	0.17	....	4.32	....	..

Total volume CO_2 equals 37.85 c.c.

Total volume CO equals 0.51 c.c.

One molar volume equals 24.4 liters at 20° C. and 750 mm.

Total weight of carbon in 37.85 c.c. of CO_2 and 0.51 c.c. of CO is 18.86 mg. 18.66/455.6 equals 4.14 percent carbon lost in the form of gases. (Graphitic carbon in sample treated equals 455.6 mg.)

Second Treatment

Bottle No.	Capacity cc.	Percent		Volume in cc.	
		CO_2	CO	CO_2	CO
7	2530	1.05	....	26.57	....
8	2560	0.13	....	3.33	....
9	2570	0.11	....	2.83	....
10	2540	0.10	....	2.54	....

Total volume of CO_2 is 35.27 c.c.

Total weight of carbon in 35.27 c.c. of CO_2 is 17.34 mg.

17.34/455.6 equals 3.81 percent carbon lost in the form of carbon gases. Total amount of carbon lost in form of carbon gases is equal to 3.81 percent, which, with percent carbon lost in first treatment makes 7.95 percent of the total carbon in the sample.

To further establish the fact that various forms of graphitic and amorphous carbon give off CO_2 when treated by the Brodie method, qualitative tests were made on various forms of carbon. Equal weights were treated with the Brodie mixture at 60° C.

for five minutes, the gases passed through saturated KI solution, and then into $Ba(OH)_2$. Comparisons of the turbidity in each case were made and found to be somewhat as follows:

Ceylon graphite	Slightly turbid
Acheson graphite	Slightly turbid
Pennsylvania graphite	Rather heavy turbidity
Calcined anthracite coal	Heavy turbidity
Coke	Heavy turbidity
Bituminous coal	Heavy turbidity

It was also found that on treating pure graphitic acid in a similar manner CO_2 was evolved.

The formation of CO_2 on treating graphite with the oxidizing mixtures indicates that the graphitic carbon passes through a series of oxidations, the final product being CO and CO_2. The oxidation of the carbon to graphitic acid with the minimum loss of carbon as CO and CO_2 takes place under rather narrow limits as to the nature of the oxidizing medium, temperature and time.

That the different graphites tested showed such a large variation in the loss of carbon as carbon gases though subjected to the same treatment led to an examination of the physical characteristics of these graphites.

The Ceylon graphite flakes when examined under the microscope were found to consist largely of grain-like, very irregular prismatic subdivisions. These prismatic subdivisions of the flake vary greatly in size and each one is seen to be composed of very thin parallel plates. Upon treatment, the oxidizing mixture penetrates between these parallel plates. The flake of Ceylon graphite also on treatment with the oxidizing mixture tends to split up into the prismatic subdivisions or permits the penetration of the oxidizing reagents into the flake between these subdivisions, thus permitting a ready access of the mixture into the flake. This is in accord with the fact that the conversion of Ceylon graphite to graphitic acid proceeds at a comparatively rapid rate, and as it is not necessary to subject this graphite to a protracted series of treatments, the loss due to the oxidation of the graphitic acid should be relatively small.

The Alabama and Pennsylvania graphites, which are very similar in structure, differ considerably from Ceylon graphite. The

flake of these graphites has no pronounced prismatic structure, but consists of relatively large thin plates that lie approximately parallel to one another in the flake. In this case, it is necessary for the oxidizing mixture to penetrate between the plates from the edges toward the center of the flake; consequently the complete oxidation of the flake requires more time than in the case of the Ceylon flake, and as the oxidation proceeds from the edges towards the center of the flake, the outer part which has been

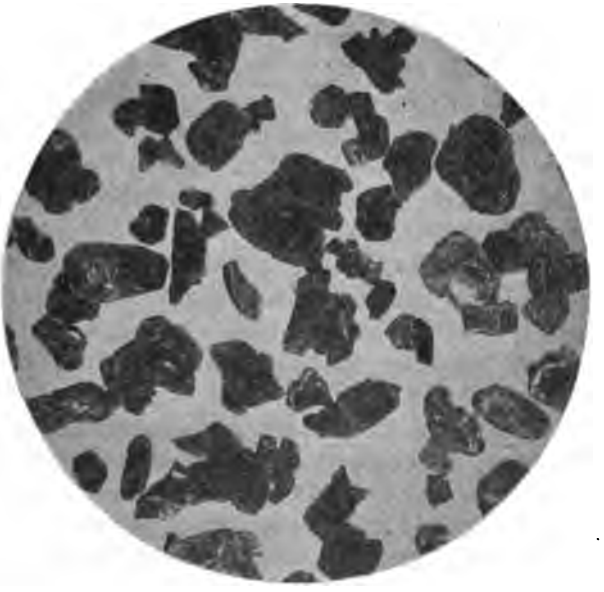

FIG. 1. Flakes of Pennsylvania graphite. (x 20.)

converted to graphitic acid is subjected to a long period of exposure to the oxidizing mixture, thus tending to greater loss through complete oxidation to CO and CO_2. No satisfactory reason can be given, however, why, when subjected to the same number of treatments, Alabama and Pennsylvania graphites give a larger loss of carbon as CO_2 than do Ceylon and Acheson graphites.

Fig. 1 shows flakes of Pennsylvania graphite magnified x 20. Fig. 2 shows flakes of Pennsylvania graphite which have been

partly or wholly converted to graphitic acid by the Brodie method, magnification x 35. It is noted that some of these flakes show very distinctly black centers consisting of the original unoxidized graphite. This illustrates very clearly that the action of the oxidizing mixture proceeds from the edges towards the center of the flake rather than from the top and bottom of the flakes. Fig. 3 shows a flake of Alabama graphite which has been completely converted to graphitic acid, magnification 200.

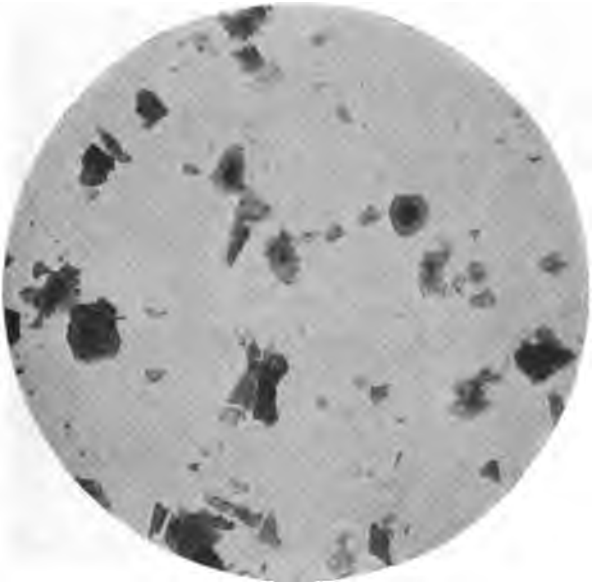

FIG. 2. Flakes of Pennsylvania graphite partly or wholly converted to graphitic acid by the Brodie method. (x 35.).

The large losses of carbon as CO_2, as given in Table IV, column 9, for Alabama and Pennsylvania graphites as compared to the comparatively smaller loss of carbon in the Ceylon graphite when given the same number of treatments with the same oxidizing mixture is difficult to explain.

The Acheson graphite which was converted readily to graphitic acid and which showed a rather small loss of carbon has no plate arrangement. This material was very finely powdered, thus permitting ready access of the oxidizing mixture to the particles.

Tests on Calcined Anthracite Coal.

Samples of Colorado calcined anthracite coal were received in which it was desired to know the percent of graphitic carbon. The samples were ground to a very fine mesh and 0.5 gm. portions treated with the Brodie mixture in the usual way. Their behavior was quite different from that of pure graphite or amorphous carbon, such as coal. The oxidizing mixture attacked the amorphous carbon content rather slowly and did not produce the

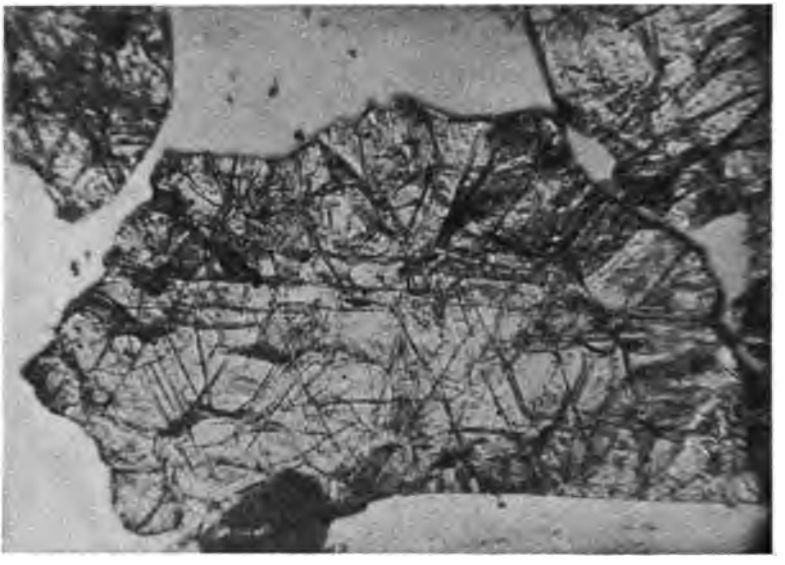

FIG. 3. Flake of Alabama graphite completely converted to graphitic acid. (x 20.).

dark reddish-brown substance characteristic of amorphous carbon, such as coal. The wash waters presented only a slight brown color and many more treatments were required to completely remove the amorphous carbon than when treating coal, the number of treatments ranging from 7 to 11. After all the amorphous carbon had been removed as indicated by the absence of color in the wash waters, the resulting products were burned in the combustion furnace for carbon content.

Real specific gravity tests were also made on the samples of calcined material and on one sample of raw anthracite from the

same district. The specific gravity and the percent graphitic carbon by combustion of the graphitic acid obtained from the samples are given in Table VIII. The densities were determined on the finely ground material by the pyknometer method, the sample being boiled with distilled water under a partial vacuum to remove all air.

TABLE VIII.

Real Specific Gravity and Graphitic Carbon Content of Calcined Anthracite Coal as Determined by Conversion of Graphitic Carbon to Graphitic Acid.

Source of Coal	Treatment	Per-cent Ash in Air-dry Sample	Spec. Grav-ity	Percent Graphitic Carbon		
				1	2	Avg.
Littell anthracite (Colorado)	Raw coal	6.68	1.41	....	....	....
	Coal treated 24 hrs. at 850° C. in gas retort	7.54	1.83	11.3	10.5	10.9
	Calcined at 920 amp..	6.93	1.79	7.9	8.1	8.0
Crested Butte anthracite (Colorado)	Calcined at 750 amp..	7.60	1.82	4.7	....	4.7
	Calcined at 920 amp..	7.86	1.82	6.1	6.0	6.0
	Calcined at 1100 amp.	8.42	1.82	15.7	17.3	16.5
Florista anthracite (Colorado)	Calcined at 920 amp..	8.82	1.79	7.3	7.2	7.2
	Calcined for 24 hrs. in gas retort at 850° C.	8.80	1.79	6.7	8.3	7.5
Anthracite (Colorado)	Calcined in gas retort, temp. unknown	8.23	1.80	7.1	6.9	7.0
	Calcined at 1100 amp	8.24	1.88	7.1	8.2	7.6

In the case of the "Littell" anthracite the specific gravity of the calcined material indicates a partial graphitization, the specific gravity of the raw anthracite being only 1.41 as compared to a specific gravity of 1.83 for the calcined material which gave the greatest amount of graphitic carbon, the specific gravity of pure graphite being 2.25 to 2.26.

In the case of the "Crested Butte" anthracite, a progressive increase is noted in the amount of graphitic carbon with the increase of amperes used in the electrical calcination. The specific gravity, however, was the same for all three of the samples.

Although artificial graphite as represented by Acheson graphite gives only a slight loss of graphitic carbon as CO_2 when oxidized to graphitic acid by the Brodie method, it is not known how great a loss of graphitic carbon due to formation of CO_2 may have occurred in the calcined anthracite given in Table VIII. If only a slight amount of graphitic carbon was oxidized to CO_2 and consequently lost the percent of graphitic carbon given may be approximately correct, however. If such a loss occurred the true percent of graphitic carbon would be higher than that indicated in the table.

As the calcined material required a large number of treatments by the oxidizing mixture, it is very probable that considerable loss of graphitic carbon occurred due to the oxidation of graphitic acid to carbon gases.

SUMMARY AND CONCLUSIONS.

1. The Brodie and Staudenmaier methods for the conversion of graphitic carbon to graphitic acid were tried on Alabama, Pennsylvania, Ceylon, and Acheson graphites, and on mixtures of Ceylon and Acheson graphites with amorphous carbon in the form of anthracite and bituminous coal and coke.

2. The Staudenmaier method was not applicable to substances containing relatively large amounts of amorphous carbon, as the reaction goes to explosive violence.

3. Amorphous carbon in the form of anthracite and bituminous coal and coke when treated by the Brodie method gave no graphitic acid in the case of the anthracite and bituminous coal, a slight amount of graphitic acid was, however, obtained from coke, this indicating the presence of graphitic carbon in coke.

4. Graphitic acid cannot be made to come to constant weight by ordinary methods of drying, as the substance is very susceptible to varying humidity changes.

5. The carbon and hydrogen content of graphitic acid can be determined by careful burning in a combustion furnace.

6. The Brodie method of conversion of graphite to graphitic acid can be hastened by a supplementary treatment with sulphuric acid and potassium permanganate.

7. Carbon in the form of coal, coke, calcined anthracite, natural and artificial graphites, gave varying amounts of CO_2 when treated with the Brodie mixture.

8. The graphitic carbon content as determined by conversion to graphitic acid by the Brodie and Staudenmaier methods and subsequent combustion gave low results as compared to direct combustion of the graphites. These differences were the least in the Ceylon and Acheson graphites and greatest in the Alabama and Pennsylvania graphites. They may be due to the differences in the physical characteristics of the graphites, such as flake structure. However, no satisfactory reason can be given, why, when subjected to the same number of treatments with the same oxidizing mixture, Alabama and Pennsylvania graphites give a larger loss of carbon as CO_2 than do Ceylon and Acheson graphites.

9. Graphitic acid when treated with the Brodie mixture slowly gives off CO_2. It appears that when graphitic carbon is treated with oxidizing mixtures such as the Brodie and Staudenmaier, a series of oxidation products result, the end products being CO and CO_2. The maximum yield of graphitic acid is obtained under rather narrow limits as to temperature, time, and oxidizing reagents.

10. With Ceylon and Acheson graphite in which the conversion of the graphitic carbon to graphitic acid proceeds at a comparatively rapid rate, the graphitic carbon content as estimated by the Brodie and Staudenmaier methods gave results which were within 5 percent of the true graphitic carbon content. On the other hand, Alabama and Pennsylvania graphites which required a prolonged treatment for conversion into graphitic acid gave very low results, due, no doubt, to a larger loss of carbon as carbon gases resulting from complete oxidation to CO and CO_2. Carbon in the form of coke and partly calcined anthracite coal though finely ground required more treatments than pure graphitic carbon in the form of Ceylon and Acheson graphites.

11. The action of oxidizing mixtures on different forms of carbon offers an extended field for further scientific investigation.

ACKNOWLEDGMENTS.

The authors gratefully acknowledge the valuable assistance and helpful suggestions received from A. C. Fieldner, supervising chemist of the Pittsburgh Station of the Bureau of Mines, and from Dr. G. A. Hulett, consulting chemist of the Bureau; also to Dr. Reinhardt Thiessen, research chemist of the Bureau, for the photomicrographs and suggestions as to the structure of graphite.

Chemical Laboratory,
Pittsburgh Experiment Station,
Bureau of Mines,
Pittsburgh, Pa., March 12, 1920.

DISCUSSION.

F. A. J. FITZGERALD[1]: This paper certainly shows excellent work by the authors. Having heard all the difficulties they had to overcome I am not surprised that I failed in making satisfactory determinations.

Most of the work was on graphitized electrodes which were made of petroleum coke. The National Carbon Co., however, also made what were, I think, known as high-grade carbons in which lampblack was used. Have any experiments been made on graphitized lampblack electrodes and, if so, how did they compare with graphitized coal? The point is this: graphitized coal and petroleum coke apparently have very different properties from graphitized lampblack.

W. A. SELVIG: I know of no such experiments that have been made. Our tests on calcined material were limited to calcined anthracite coal.

C. H. BIERBAUM[2]: The problem of determining the percentage of graphitic carbon in a mixture of graphite and amorphous car-

[1] FitzGerald Laboratories, Inc., Niagara Falls, N. Y.
[2] Consulting Engineer, Buffalo, N. Y.

bon has long been known as an exceedingly difficult problem and it has been fully appreciated that the developing of a practical method for this determination would involve tedious and painstaking work. The results given in this paper are very encouraging and reflect a great deal of credit upon the investigators.

There seems to be one matter in these investigations, however, which has not been fully considered, namely, what became of the mica in at least two of the four graphites treated? Cannot the discrepancy between Pennsylvania and Alabama graphite and the other two graphites in Table IV be accounted for by the presence of this mica?

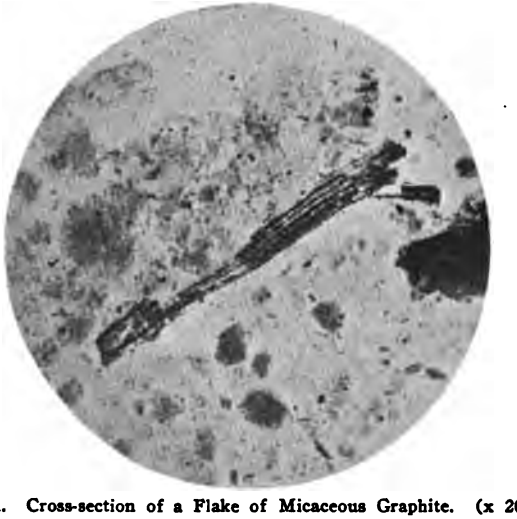

FIG. A. Cross-section of a Flake of Micaceous Graphite. (x 200.).

Ceylon graphite has appeared on the American market in two distinct varieties, namely, the micaceous or flake form, and in the crystalline or columnar form. The percentage of ash given in Table III identifies this Ceylon graphite here under consideration as the crystalline, columnar or non-micaceous variety, leaving the Pennsylvania and Alabama graphites of the four graphites tested as the usual micaceous variety; their low percentage of ash, however, shows that they were very pure samples.

In the discussion of the Ceylon graphite, on page 143, the statements are rather conflicting. Properly speaking, Ceylon graphite which is not of the micaceous variety should not be spoken of as

having flakes. The two kinds of Ceylon graphite which are sold on the American market can be readily distinguished under the microscope. The micaceous one is made up of alternate layers of mica and graphite of varying thickness and is very similar to that of the Pennsylvania, Alabama, Ticonderoga, and numerous other American flake graphites. Fig. A is a photomicrograph of a cross-section of a flake of micaceous graphite, the alternating

FIG. B. Surface of a Flake of Ticonderoga Micaceous Graphite. (x 100.)

layers are composed of graphite and mica, the mica being the translucent layer. The entire lustre of all micaceous graphites is due to the presence of laminæ of mica, and therefore they should not be classified as a crystalline graphite, since the individual layers of the graphite are amorphous in character. The crystalline Ceylon graphite is practically identical with the crystalline graphite as found in Dillon, Montana. It is of bituminous origin.

Fig. 1 in the paper, showing the flakes of Pennsylvania graphite, is a typical field of graphite flakes of the micaceous form. It even suggests the cleavage in the plates of mica. The same is true of Fig. 3, showing the remaining mica of Alabama graphite. It is impossible to imagine that this mica, which the photograph identifies as muscovite, should have been "completely converted to graphitic acid."

The flake of mica as shown in Fig. 3 in this paper may be considered as identical with photomicrograph B, which is the sur-

FIG. C. Surface of a Flake of Alabama Micaceous Graphite. (x 100.).

face of a flake of Ticonderoga micaceous graphite. They both show the prevailing 60° angle of cleavage in the muscovite mica. The same is true of Fig. C, showing the surface of a flake of micaceous Alabama graphite; also built up in a manner of Fig. A, in alternate layers of mica and graphite. Many micaceous graphites contain a very high percentage of very pure mica and the ash still shows the exact structure of this mica in those cases where the impurities during the incineration have not caused the fusing of the mica. Fig. 2 in the paper also shows the effect of the mica plates on the outside of the flake. The oxidizing effect

had to enter between the plates of mica at the edges and for that reason the oxidation of both the Pennsylvania and Alabama graphites is much slower than the other two forms of graphite tested.

W. A. SELVIG: In referring to Fig. 3 as a flake of Alabama graphite completely converted to graphitic acid, the authors did not mean that mica or similar mineral originally present in the graphite had been converted into graphitic acid, but that all of the carbon had been oxidized.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

EXAMPLES OF SELECTIVE ADSORPTION BY B. PYOCYANEUS.[1]

By WILLIAM C. MOORE.[2]

ABSTRACT.

A study of the adsorption of hydrochloric, sulphuric and acetic acids by the bacillus pyocyaneus, alone and in the presence of sodium chloride, showing that selective adsorption occurs which is partly physical and partly chemical in its nature; part of the acid is taken up in a free molecular condition. It is shown that the bacteria suspended in water between electrodes migrate toward the anode, indicating that they carry a negative charge. Donnan's theory of "Membrane Equilibria" is used to explain this negative charge. [J. W. R.]

INTRODUCTION.

It has long been known that many bacterial species are "agglutinated" or flocculated by acids within certain ranges of hydrogen ion concentration, the actual effective value for agglutination apparently differing with the different organisms. Thus it was found by Michaelis[3] and his co-workers[4] that in certain acetic acid sodium acetate mixtures typhoid bacilli were strongly agglutinated while colon bacilli and paratyphoid A and B were unaffected. Michaelis' proposal to use this phenomenon as means of identification of typhoid bacteria, however, has never been

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[3] Folia Serologica (1911), 7, 1010-1012.

[4] Zeit. Immunitätsforsch (1912), 12, 310.

widely accepted, since agglutination with specific serum is more readily performed. Previous to the work of Michaelis, it was shown by Buxton and his co-workers[5] that adsorption plays an important, if not the essential part, in the agglutination of bacteria by acids, and by certain artificial dyestuffs. Bordet[6] assumed that in the specific agglutination of a bacterium in the presence of sodium chloride, the second stage of the process consists in the adsorption of salt with the result that the electrical charge on the bacteria is neutralized and the bacteria thus agglutinated. Joos[7] has shown qualitatively that such adsorption takes place. Adsorption phenomena have, therefore, long been recognized as playing an important part in agglutination. If sodium chloride is adsorbed when it is present in specific agglutination, to what extent is the agglutinin itself adsorbed? Again, what is the real nature of the agglutination process and on what does it depend? Believing that some light on the solution of these problems might be obtained by a study of the conditions involved in the agglutination of bacteria by inorganic substances, an investigation of this field has been undertaken. The work presented in the present paper concerns the adsorption of certain acids by B. pyocyaneus, and is given here because of its interest from a physico-chemical standpoint.

EXPERIMENTAL.

The general method of procedure was to make cultures of the organisms on beef extract (or infusion) agar in Kolle flasks, wash off the culture in distilled water, wash the bacilli four or more times with distilled water, re-suspend them in distilled water, and filter through coarse filter paper to remove clumps and particles of culture medium.

A migration experiment with an aqueous suspension of B. pyocyaneus, prepared as above, was now carried out using a U-tube of the Burton[8] type. Under the influence of 110 volts direct current, the bacteria migrated toward the anode, thus indicating that they carried a negative charge.

[5] Zeit. Phys. Chem. (1907), 57, 47-89; *ibid.*, 60, 469-506.
[6] Ann. de l'Inst. Pasteur (1899), 13, 225.
[7] Zeit. für Hygiene (1901), 36, 422-439.
[8] Burton: "Physical Properties of Colloidal Solutions" (1916), 131.

In the preliminary experiments, a qualitative study of the action exhibited by B. pyocyaneus toward alizarin red was made. It was found that suspensions of B. pyocyaneus which had been thoroughly washed with water and allowed to stand in contact with the water were decidedly alkaline in reaction. When centrifuged, the bacteria carried down part of the dye, which, however, could be removed by two washings with distilled water. On adding water and alizarin red to this centrifuged mass, the reaction was at first neutral, slowly becoming more alkaline. In the presence of N/500 sulphuric acid, a certain experiment showed the bacteria to be alkaline in reaction, while the supernatant fluid was decidedly acid. This held true when the number of bacteria per cubic centimeter was varied from about 5×10^8 to 40×10^8.

Using a different organism, B. proteus vulgaris, it was found that alizarin red is more difficult to remove from the bacteria after they had been previously treated with acids than before being subjected to such treatment. Even when the acid employed was of such a concentration that the bacteria at first showed an acid reaction, subsequent washing with water gave a bacterial sediment alkaline in reaction.

In the presence of sodium chloride, B. pyocyaneus, while still alkaline to alizarin red, took on a deeper shade of color than when treated with water alone.

After a series of preliminary experiments, accurate quantitative data were now obtained on the adsorption by B. pyocyaneus of (1) sodium chloride, and (2) hydrochloric, sulphuric and acetic acids, both in the presence and the absence of sodium chloride. The experiments on sodium chloride in the presence of acids are not reported here, as the results obtained were irregular and must be subjected to further study. In this work suspensions of the bacteria, prepared as described above, were used. In carrying out an experiment, a definite volume of the acid or the sodium chloride solution was run into a large centrifuge tube, then a definite volume of the bacterial suspension was added. Preliminary experiments having shown that considerable evaporation occurs during an experiment of this kind, the tubes

in any one series of experiments were quickly weighed, the contents of each tube thoroughly shaken, and the tubes placed in an incubator at 37.5° C. for an hour. On removal from the incubator any agglutination occurring was noted, and the tubes then set in an ice-box over night. The next day each tube was centrifuged until the supernatant liquid was practically clear, and then weighed. By this means a sufficiently accurate measure of the evaporation of water from the tube was obtained, as the weight difference in grams was assumed to be equal to the number of cubic centimeters of water lost by evaporation. This assumption could, of course, be safely made, as volumes were read only to the nearest hundredth of a cubic centimeter, and all measurements were made at room temperature.

A definite volume of the clear, supernatant fluid was now withdrawn and the acid content determined by titration with sodium hydroxide. With hydrochloric and sulphuric acids, methyl orange was the indicator used; with acetic acid, phenol-sulfone phthalein. To determine chloride ion, tenth-normal silver nitrate was used, with potassium chromate as indicator. When both acid and chloride were to be determined, the acid was first determined and then the chloride in the neutralized solution.

By evaporation of a definite volume of the original washed suspension of bacteria, at 70° C., a residue was obtained, the weight of which gave the amount of bacterial substance present. A count of the bacteria per cubic centimeter in the original suspension was also made with a Levy hemocytometer.

The following protocol will serve as an example of the method of work:

Experiment 25.

A three-day-old culture of B. pyocyaneus was suspended in distilled water, washed four times, re-suspended in water, filtered and used in the following protocol with hydrochloric acid. Bacterial count, 3.77×10^9 bacilli per cc. On evaporation of 10.22 cc. to dryness at 70° C., 1×10^{-3} grams of bacterial substance per cc. was obtained.

After mixing the bacteria with the acid, the tubes were incubated one hour at 37.5° C., then set aside in the ice-box over night. They were centrifuged and the acid in 10.22 cc. of the supernatant liquid titrated.

TABLE I.

Detailed Protocol: Adsorption of Hydrochloric Acid by B. Pyocyaneus.

Tube No.	1	2	3	4	5	5
Bacterial Suspension, c.c.	5.00	5.00	5.00	5.00	5.00	5.00
N/20 HCl. (Factor 0.9388) c.c.	8.00	4.00	2.00	1.00	0.80	0.60
H_2O, c.c.	7.00	11.00	13.00	14.00	14.20	14.40
Final conc., HCl, 0.9388 ×	0.02 N	0.01	0.005	0.0025	0.002	0.0015
Weight on mixing, grams	113.27	104.57	111.85	110.58	114.54	115.28
Weight, centrifuged, grams	112.33	103.42	111.00	109.64	113.80	113.81
Loss of Weight, grams	0.94	1.15	0.85	0.94	0.74	1.47
Final Volume, c.c.	19.06	18.85	19.15	19.06	19.26	18.53
Calc. NaOH for No Action, c.c.	70.92	35.46	17.73	Spoiled	7.09	5.32
Observed c.c., NaOH.	69.19	33.10	14.60	.....	4.78	0.00
Adsorbed Acid, equivalent to NaOH, c.c.	1.73	2.36	3.13	.....	2.31	5.32
Total Acid Adsorbed, × 10^6 moles, c.c.	8.86	12.08	16.03	.....	11.83	27.2
Percent Acid Adsorbed	2.44	6.65	17.60	.....	32.57	100.0
Acid Adsorbed × 10^6 moles per 10^{10} bact.	4.75	6.47	8.59	.....	6.34	14.40
Acid Adsorbed × 10^6 moles per gram dry bact.	1.77	2.41	3.20	.....	2.36	5.44

The results obtained are shown in summarized form in the following Tables:

TABLE II.

Adsorption by B. Pyocyaneus of Sodium Chloride.

Original Salt Conc.	29	60	89	119	147	175	238	263	350	Amount Bacteria per cc.
Salt adsor'd (a)	—186.0	0	0	—97.0	0	0	—150	0	—1027.0	4.4×10^9
Salt adsor'd (b)	14.5	0	0	—7.5	0	0	—11.5	0	—78.9	1.145×10^{-3}

Salt concentration expressed in milli-equivalents per liter. Line (a) shows salt adsorbed in moles$\times 10^6$ per 10^{10} bacteria; line (b) salt adsorbed in moles × 10^6 per gram of bacterial substance. (—) means "Negative adsorption."

In Table II the figures given show that sodium chloride in concentrations from 29 millimoles per liter up to 350 millimoles per liter is not adsorbed by B. pyocyaneus. In fact, there is some negative adsorption, *i. e.*, in the presence of salt, at certain concentrations, water is taken up by the organisms.

TABLE III.

Adsorption by B. Pyocyaneus of Acids from Aqueous Solutions.

Concentrations Used	1.0	1.50	2.0	2.50	5.0	10	20	Amount Bacteria per cc.
H_2SO_4; factor 1.0229 (a)	2.93	2.47	3.03	13.77	5.35	9.60	3.23	*1.35×10^9
H_2SO_4; factor 1.0229 (b)	1.10	0.93	1.14	5.81	2.25	4.05	1.36	*1.6×10^{-8}
HCl; factor 0.9388 (a)	2.96	14.4	6.34		8.59	6.47	4.75	3.77×10^8
		3.78	3.54	3.44	3.62	2.59	0.86	5.29×10^9
HCl; factor 0.9388 (b)	1.79	5.44	2.36		3.20	2.41	1.77	1×10^{-8}
		2.32	2.13	2.07	2.18	1.56	0.52	0.88×10^{-8}
$HC_2H_3O_2$ factor 1.153 (a)	17.60	17.0	21.6	26.2	41.2	15.80	89.6	0.824×10^9
	4.8	3.26	3.49	7.46	6.66	†8.79	9.66	2.64×10^9
$HC_2H_3O_2$ factor 1.153 (b)	2.14	2.06	2.62	3.17	5.0	1.91	10.9	0.68×10^{-8}
	2.88	1.92	2.10	4.49	4.0	5.28	5.80	0.44×10^{-8}

Figures at head of columns express concentrations in milli-equivalents per liter. Lines (a) and (b) have the same significance as in Table II.

* For concentrations 1.0, 1.5 and 2.0 the figures were the same as for the hydrochloric acid—3.77×10^9.

† Concentration was 8, and bacterial dosage twice that in other tubes. Volume was 25 cc.

Table III shows that with hydrochloric, sulphuric and acetic acids there is definite, positive adsorption of the acids concerned, at every concentration studied. This adsorption, based on the amount adsorbed per gram of bacterial substance, is of the same order of magnitude for the three acids, and in each case at least one maximum of adsorption is shown. Similarly, in Table IV it is seen that in the presence of sodium chloride adsorption still occurs and maxima of adsorption are still present. However, a comparison of Tables III and IV shows that the general tendency of sodium chloride is to decrease the amount of adsorption of

sulphuric acid, and acetic acids, and possibly to increase it with hydrochloric.

TABLE IV.

Adsorption by B. Pyocyaneus of Acids from Sodium Chloride Solution.

Concentrations Used	1.0	1.5	2.0	2.5	5.0	10.0	20.0	Amount Bacteria per cc.
H_2SO_4 (Factor 1.0229) (a)	5.14	5.80	6.08	7.20	6.86	4.24	3.06	2.04×10^{9}
H_2SO_4 (Factor 1.0229) (b)	1.12	1.26	1.32	1.56	1.49	0.91	0.66	9.4×10^{-4}
HCl (Factor 0.9388) (a)	10.50	12.20	15.00	13.20	15.20	9.70	9.10	2.04×10^{9}
HCl (Factor 0.9388) (b)	2.28	2.64	3.27	2.87	3.31	2.11	1.95	9.4×10^{-4}
$HC_2H_3O_2$ (Factor 1.153) (a)	. . .	. . .	16.60	18.60	5.58	15.60	5.72	0.824×10^{9}
$HC_2H_3O_2$ (Factor 1.153) (b)	. . .	. . .	2.02	2.26	0.67	1.89	0.69	0.68×10^{-4}

Figures at heads of column and (a) and (b) have same significance as in Table III.

Sodium chloride present; with H_2SO_4, 0.147N; with HCl, 0.147N; with $HC_2H_3O_2$, 0.1456N.

In Tables II, III and IV, inclusive, the total volume employed was 20 c.c.

DISCUSSION OF RESULTS.

The three possible types of action when bacteria are mixed with an acid are:

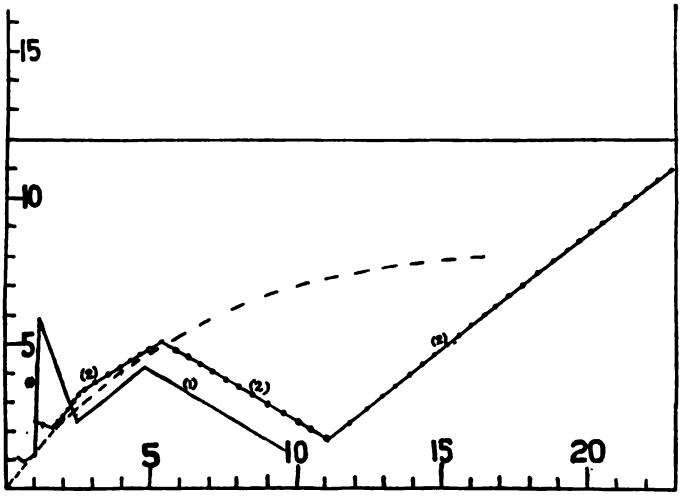
1. Simple adsorption. This may be (a) of the molecular acid, or (b) of the ions of the acid, or (c) of a mixture of molecules and of ions.

2. Chemical combination of the acid, as a molecular species, or of its ions, with the protein of the bacterial substance.

3. Catalytic hydrolysis of the protein. This type of action is probably largely due to the hydrogen ions present. If carried to an extreme it would result in the formation of free amino acids capable of neutralization by sodium hydroxide, thus giving an increase in the titrable acid present.

We shall now discuss the above possibilities in turn.

The modern view of adsorptive processes is that chemical forces hold the adsorbed substance on the surface of the adsorbent.[9] A chemical action of this type would be different from that of type 2, in that the action would be limited to the surface involved. As protoplasm is colloidal in nature, the internal surfaces of the bacterial bodies are probably very great in extent as compared with the external surface. Due, however to the small size of the organisms, any one of the suspensions we have used exhibits a



LEGEND FOR FIG. 1.

Abscissa, concentration of acid employed in millimoles per liter. Ordinate, adsorption per gram of bacterial substance in millimoles. Curve 1, for sulphuric acid. Curve 2, for acetic acid. The dotted curve indicates the general type of curve exhibited by the "adsorption isotherm."

very considerable external surface as the following calculation shows: Park and Williams[10] give the dimensions of B. pyocyaneus as 0.6 μ, to 1.0 μ thick and 2 to 6 μ long. Taking the average diameter as 0.8 μ and the average length as 4 μ, the external surface for a single organism, regarding it as a cylinder, is 1.1×10^{-7} sq. cm. In one of the experiments with sulphuric acid, 5 cc. of a suspension containing 1.354×10^{9} bacteria per cc. was used. The number of organisms involved was therefore $5 \times$

[9] Langmuir: J. Am. Chem. Soc. (1917), 39, 1848-1906.
[10] "Pathogenic Micro-organisms" (1914), 383.

1.354×10^9 or 6.77×10^9. The total superficial area of the bacteria in this experiment is therefore $6.77 \times 10^9 \times 1.1 \times 10^{-7}$ or approximately 750 sq. cm. This is probably only a small part of the total area, internal and external, available for adsorption. Simple adsorption of this type should theoretically follow the course of a curve similar to the well-known "adsorption isotherm." The results obtained in this paper do not follow such a curve, as may be seen by an inspection of Fig. 1, where the dotted curve indicates, roughly, the course of an adsorption isotherm.

Chemical combination due solely to the available hydrogen of the acids employed will not explain the results we have obtained. For example, in one experiment cited in Table III, 5.81×10^{-8} moles, or 11.62×10^{-3} equivalents of sulphuric acid were taken up by 1 gram of bacterial substance. This means that 11.62 equivalents of acid would "neutralize" 1,000 grams of bacterial substance, and hence the equivalent weight of bacterial substance in this instance would be 1,000 divided by 11.62 or 86.06. In order for a protein to exhibit as low an equivalent weight as this, it would have to be completely hydrolyzed into its constituent amino acids. Indeed, of the amino acids making up the proteins,[11] alanin, $C_3H_7NO_2$ is the acid having a molecular weight nearest 86.06, and no protein is known which is built up solely from this substance. Again, in order to accomplish any great degree of hydrolysis of a protein, much more concentrated acids must be used than we have employed in this work.

Combination of the molecular acids employed, however, does not involve any of our ordinary conceptions of valence. Moreover, with acids differing as widely in activity as hydrochloric and acetic, the order of magnitude of the amount of acid adsorbed per gram of bacterial substance is the same. This is strongly indicative of the molecular substances themselves being involved in the action of the acids on the bacterial bodies. It cannot be simple adsorption alone, though this is not precluded. The evidence here presented would seem to indicate that both adsorption and chemical combination take part in the action of acids on B. pyocyaneus.

With respect to the catalytic hydrolysis of the protein substance in the bacteria, such hydrolysis is ordinarily accomplished by boil-

[11] Robertson: "Physical Chemistry of the Proteins" (1918), 6.

ing with a concentrated acid. The possibility is not excluded, however, of hydrolysis of this type taking place in dilute solutions, at a low rate. It would therefore be the greater the more concentrated the acid solution employed, and, as it results in the splitting of proteins into free amino acids, would give an increase in the titrable acid—an apparent decrease in the amount of acid adsorbed in the higher concentrations of acid.

The alkaline reaction of an aqueous suspension of B. pyocyaneus, and the increase in alkalinity of such a suspension on standing after thorough washing with water, indicates another type of hydrolysis, explicable by Donnan's theory of "Membrane Equilibria.[12] According to this theory, if a constituent of the cell ionizes into a non-diffusible organic radical R^-, and a positive radical M^+, M^+ and OH^- from the water within the cell diffuse out of the cell into the water, leaving H^+ and R^- within the cell. We know, however, that in the case of the proteins HR is a weak acid, so the hydrolysis would in all probability be greater than demanded simply by Donnan's theory. That the OH^- ions are present on the surface of the bacterial cells, may be the cause of the cells in aqueous suspension carrying a negative charge of electricity.

The Tables may now be briefly discussed. The maxima of adsorption shown by sulphuric, hydrochloric and acetic acids in Tables III and IV indicate that in their action upon B. pyocyaneus simple adsorption is not entirely responsible for the results obtained. This, and the calculations above, from the basis of the conclusion that chemical forces help determine the amount of acid adsorbed per gram of bacterial substance.

The exact location of these maxima may not be of significance, but if we express the original concentration of the sulphuric acid employed in molar instead of equivalent quantities, it is seen that one of its maxima coincides with that of hydrochloric and acetic acids. (See also Fig. 1.) This again suggests the participation of molecular substances in the reaction.

No adequate explanation of the effect of salt on the adsorption of the acids has offered itself. It is of course possible that it

[12] See the interesting discussion in Vol. II, Lewis' "System of Physical Chemistry" (1919), 275.

decreases the degree of dissociation of the hydrochloric acid, causing an increase in the adsorption of the molecular substance, and that its ions react to some extent with the sulphuric acid forming some sodium hydrogen sulphate and lessening the amount of free sulphuric acid available for adsorption; but with a weak acid like acetic such an explanation is not tenable.

Its action in increasing the adsorption of water does not at present yield to any simple explanation. In amount, the greatest excess found was where 0.35 molar salt was used, the excess being 78.9 millimoles per gram of bacterial substance. The total salt present was found to be equivalent to 92.18 cc. tenth-normal silver nitrate, the calculated amount being 87.66 cc., an excess of 5.15 percent. As the evaporation was taken into account by weighing, any change in volume due to compression of the water in its adsorption on the bacteria could not be ascertained in this way. This whole question of the action of salt is to be gone into much more thoroughly than we have at present done.

SUMMARY.

In conclusion, this paper shows that:

1. Treatment of B. pyocyaneus with hydrochloric, sulphuric and acetic acids, alone and in the presence of sodium chloride, results in selective adsorption of the acids employed, in that the adsorption found does not follow the adsorption isotherm.

2. The adsorption is partly physical and partly chemical in nature.

3. In the adsorption, part of the acid is taken up in a free molecular condition.

4. Sodium chloride is not readily adsorbed by B. pyocyaneus.

5. An application of Donnan's theory of "Membrane Equilibria" is made to explain the alkalinity of suspensions of B. pyocyaneus in water, and to explain the negative charge on these organisms.

DISCUSSION.

W. C. MOORE: I will just take a few minutes to explain why we began this work, and say something as to what it means. If you take an animal like a rabbit or a guinea pig, and give such an animal by means of several injections, either intravenously, interperitoneally or subcutaneously, suspensions of certain species of germs, as typhoid, or any other individual species, you will find that the serum of the blood taken a week or so after the last injection will precipitate out, even in very high dilutions, the specific bacterium that you use for the inoculation of the animal. This phenomenon is known as agglutination. Since the bacteria themselves are so small, they behave really as suspensoid colloids; and the bacterial bodies being composed of protoplasm, which we know is an emulsoid colloid, the problem of determining just how and why the agglutination of bacteria takes place by the specific serum which is developed by using certain definite bacteria is of interest from a colloid standpoint. The thing we are most interested in is to find out why it is that a rabbit made immune to typhoid will give a serum which will not agglutinate other bacteria, and why a rabbit or other animal made immune to certain other bacteria, as for instance pyocyaneus, will not agglutinate typhoid bacteria. The first thing we ran against was this phenomenon known as acid agglutination. I found that a great deal of experimental work had been done by Michaelis[1], but it was not of such a type that you could follow the reaction. We therefore started out with several species of micro-organisms: typhoid, colon, this particular pyocyaneus, and another bacillus known as proteus vulgaris, but found that pyocyaneus was a little more convenient to study than any of the others. In the first place it is easily grown; in the second place, it is easily handled and is not particularly dangerous unless you get it in an open wound; and in the third place, in washing it in distilled water, you can centrifuge the bacteria to the bottom of the vessel very quickly. If you take a culture of this particular bacillus and suspend it in distilled water, you can wash it four or five times in as many hours, almost completely or practically completely free

[1] Folia Serologica (1911), 7, 1010-12.

of salt. If you take certain other bacteria, for instance the colon bacillus, it sometimes takes as long as a week to completely wash that organism free of salt, because it settles at a very slow rate. That is how and why we began the work. As far as experimental details are concerned, some points have come up since the paper was in print, which are even more important from the colloid standpoint than the paper itself. In the first place, no reference is made in the actual paper to the agglutination phenomena themselves. We purposely left out the order of agglutination in these experiments, because we did not know enough about the results we were getting to commit ourselves. We do not know much more now, but some of the results are of interest. If you will note the table which is given, you will find that the order of adsorption of these acids is sulphuric, acetic and then hydrochloric. Since the paper was printed, we have carried out some experiments with this same bacillus with oxalic acid and find that it comes in between acetic and hydrochloric. When we study bacterial agglutination, we find that flocculation in these experiments follows directly the degree of dissociation of the acid: that is hydrochloric acid flocculates these bacteria most; then sulphuric acid, then oxalic acid and then acetic acid. When we found that out we went on with the colon bacillus, and got some exceedingly interesting results. Instead of following the order here, the colon bacillus followed the order of the degree of dissociation of the acid in the amount of the adsorption. There was most hydrochloric adsorbed; then oxalic, then acetic. However, with the flocculation, the sulphuric flocculated most, then oxalic, then acetic, and finally the hydrochloric. When we arranged the results in that order, it was plain to see what had happened; the colon bacillus apparently had an iso-electric point which is slightly on the alkaline side of neutrality, and in using hydrochloric, sulphuric and oxalic acids, the hydrogen ion concentration is sufficiently great so that the bacteria are peptized. The negative ions of sulphuric and oxalic precipitate these positively charged particles, because these ions are di-valent, and have a precipitating power much greater than you can have in the case of the negative ions of hydrochloric and acetic acid. Acetic, being a weak acid, barely neutralizes the bacterial charge and hence gives more com-

plete flocculation than hydrochloric, which very strongly peptizes the bacteria.

W. D. BANCROFT[2]: You will please note that colloid electrochemistry includes pretty nearly everything from wood pulp through electrodes to the inoculation of rabbits. This paper is before you for discussion. I would like to ask whether you imagine that quantitatively the action is proportional to the electrolytic dissociation, or whether it is simply qualitatively?

W. C. MOORE: It is closely qualitatively, so far as we know.

W. D. BANCROFT: That is what I thought it must be.

[2] Professor of Physical Chemistry, Cornell University.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

THE SÖDERBERG SELF-BAKING CONTINUOUS ELECTRODE.

By Joseph W. Richards.[1]

Engineer C. W. Söderberg,[2] residing in Christiania, Norway, imagined over ten years ago a self-baking electrode, formed continuously from soft carbon mixture, which would be baked in the same furnace in which it is used and thus provide a continuous electrode.

The first electrode of this kind was built by Mr. Söderberg in 1909. He naturally met with many difficulties in developing his idea, and it was not until 1915 that he actively pushed the development of this electrode, in connection with the company with which he is now engineer.

After considerable development work, the company succeeded in overcoming in a practical manner all of the difficulties, and in November, 1918, a 400-millimeter (16-inch) electrode was operated on a ferro-manganese furnace without disturbances to the furnace and with no fracturing of the electrode. Since that time electrodes of all sizes up to 850 millimeters (34-inch) diameter have been successfully operated, both in open and closed furnaces, in making ferro-silicon, silico-manganese and ferro-molybdenum.

GENERAL DESCRIPTION.

This electrode may be in general described as embodying the idea of feeding continuously unbaked electrode mixture to the furnace, the mass being baked by the heat of the furnace in which it is being used, and the apparatus being so arranged and worked that the operation is practically continuous during the life of the furnace. The idea therefore entirely dispenses with the use of previously-baked electrodes and with their replacement or intro-

[1] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa. Manuscript received October 16, 1919.

[2] Engineer, Det Norske Aktieselskab for Elektrokemisk Industri. (Electrode subject of Application for U. S. Patent.)

duction from time to time in the furnace. In operation, the baked end of the Söderberg electrode is always in the furnace, while the unbaked part is outside and can be lengthened from time to time as the electrode is consumed.

The heat necessary to bake the mass is all conducted from the lower, baked end, or contributed by hot gases or radiation, or partly derived from the passage of current through the baked part.

FIG. 1. General View, showing cemented filling chamber.

The electric current is best introduced at the lower or baked end of the electrode, where the hot carbon has become conducting, but may, in small electrodes, be introduced higher up if an iron casing is provided to carry the current from the unbaked part to the baked part of the lower end. In usual practice the movable electrode holder is placed near the top or roof of the furnace, and encircles the iron casing in which the electrode mixture is encased. The baking takes place comparatively close to the furnace, usually at a small distance above the electrode holder, when

the latter is in its usual position encircling the electrode close to the furnace.

If the design of the furnace requires it, the electrical connection may be made higher up, or further from the furnace, especially with smaller electrodes, but in this case the iron shell must be heavy enough to carry the current past the unbaked mass to the baked and conducting part of the carbon electrode.

The casing is thus an important part of the electrode system. It may be made as a thin casing merely surrounding the electrode or as an exterior shell provided with interior projecting ribs, which latter strengthen the structure and add to the longitudinal conductivity of the electrode as a whole. The casing has, further, the function of holding the electrode shape and size while new mixture is being added; also of protecting the carbon from exposure to the air and consequent combustion before it enters the furnace. It also facilitates the transfer of electric current, with small loss, from the holder to the electrode, because of the good electrical contact of metal to metal, and further distributes the current to the carbon with which it is in very intimate contact over a large surface. It also stiffens and reinforces mechanically the unbaked part of the electrodes. It should be strong enough to keep its shape during the stamping in of fresh electrode mixture.

The writer spent some time, in August, 1919, inspecting the operation of a Söderberg electrode at Fiskaa, near Christiansand, Norway, where the following observations were made:

The whole operation of construction and working of a Söderberg electrode may be considered under the following headings:

1. Preparation of the electrode mixture.
2. Design and construction of the iron casing.
3. Lengthening the electrode by adding new sections of casing.
4. Stamping fresh electrode mixture into new sections.

1. PREPARATION OF ELECTRODE MIXTURE.

The raw electrode mixture is practically the same as is used in ordinary carbon electrodes which are to be baked. The ingredients consist of coke, anthracite, tar and pitch, all finely ground and mixed together in the usual proportions at a temperature of about 80° C. (176° F.).

In order to obtain a higher conductivity in the baked carbon, the anthracite used is preferably semi-graphitized. This is done by heating it in an electric furnace of the usual type for this purpose.

The grinding of coke and anthracite is done in any suitable form of mill. An enclosed mill of the Raymond air blast type is to be recommended for this purpose. The fineness is that usual in ordinary electrode manufacture.

FIG. 2. Close-up, showing details.

The mixing with pitch and tar is done in the usual manner in a heated mixing machine, of which several efficient models are on the market. A heated roller crusher may be used for this operation, but is not so efficient.

If the mixture is allowed to cool, it must be re-heated to about 80° C. (176° F.) before it can be stamped into the electrode. This re-heating can be done in the mixing machine or in a specially designed electric oven of simple construction, placed near the point of use.

The making of a metric ton (2,200 lb.) of electrode mixture would require about the following labor:

Boiling of tar	6 man-hours
Crushing and grinding	7 " "
Mixing and storing	8 " "
Total	21 man-hours

In a large plant, with best labor-saving appliances and most modern machinery, this labor cost can probably be considerably decreased.

2. CONSTRUCTION OF THE IRON CASING.

The iron casing is made in sections of suitable length, which varies with the size of the electrode and the conditions of its use. Each section is made alike, and new ones are riveted or welded to the old ones to elongate or extend the electrode.

The individual sections are constructed of several longitudinal segments which are bent at a right angle so that one part forms part of the wall of the section while the other part projects inwardly towards the center of the circular section, forming a rib or partition which will extend into the electrode mixture. These partitions are pierced with holes or "ports" to keep the mixture united through the ribs, and thus prevent its separation or cleavage from the sheet-iron partitions. The outer shell is pierced with numerous holes, which are punched, chiseled or drilled, to allow free escape for tar vapors.

With the contact holder clamped close to the furnace, thin sheet iron is used for the casing, 0.5 to 0.9 mm. thick (20 to 26 gauge). With smaller electrodes and the air-cooled holders clamped to the upper part of the electrodes, sheet of 0.9 to 1.5 mm. thickness is used (16 to 20 gauge). In the latter case, the iron has sufficient cross-section to carry the whole current. The 850 mm. (34-inch) electrode seen in operation at Fiskaa was carrying 23,500 amperes, at an average current density of 4.2 amperes per square centimeter. The cross-section of the carbon in this electrode is 5,670 square centimeters and that of the iron 77 square centimeters. The iron alone should be able when cold to conduct all of this current without serious heating, making the electrical conductance of the cold electrode virtually independent of the carrying power

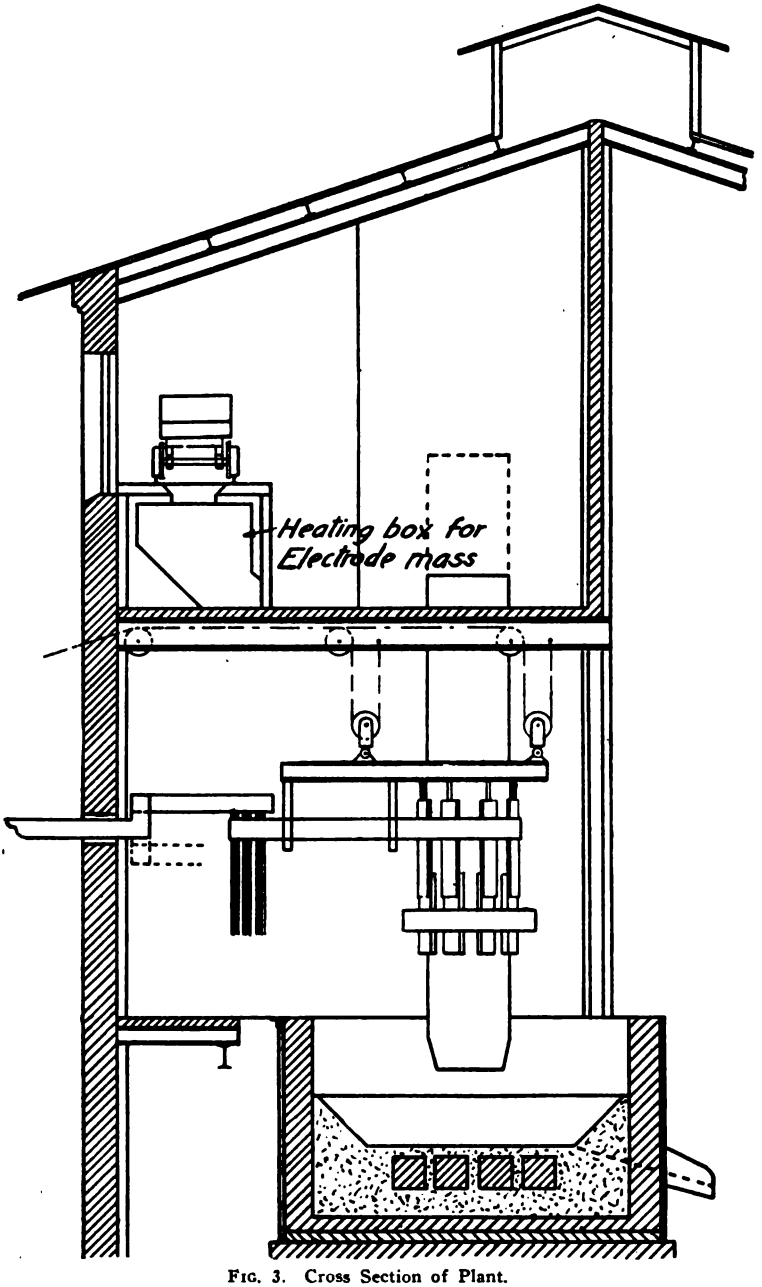


FIG. 3. Cross Section of Plant.

of the carbon mass, *i. e.*, whether it is baked or unbaked where current is passing.

Such casings are made in an ordinary machine shop, without special machinery of any kind. The labor required amounts approximately to 29 man-hours per meter of casing or 34 man-hours per ton of baked electrode carbon in the electrode.

3. LENGTHENING THE ELECTRODE.

When in use, the upper or outer end of the electrode is lengthened from time to time in proportion as the lower end is consumed. This is done by adding a section of sheet-iron casing and stamping it full of raw electrode mixture.

A stamping platform or enclosed room must be provided around the upper end of the electrode, when it is in a vertical position, to protect the workmen from the gases and heat of the furnace. At Fiskaa this took the form of a small room built of reinforced concrete and entirely closed except for a door to the outside and a chimney for ventilation passing through the roof. (See sectional view of plant.) The electrode passes through the floor of this room through a stuffing box made tight by asbestos packing, rendering the room entirely free from dust and smoke. The room was not unpleasantly warm to stay in or to work in. With tilting furnaces this room or chamber can be built fixed, and sliding doors or shutters provided which allow the electrode to swing with the furnace when it is tilted and to come back into the chamber when the furnace returns to normal position.

The operation of lengthening the electrode consists of placing a new section of iron casing on top of the electrode and either bolting, riveting or welding it into position, the latter either electrically or with the oxy-acetylene blowpipe flame. The practice is well organized and effective, but it is probable that still further improvements may be made in these details as the method is further developed.

4. STAMPING FRESH ELECTRODE MIXTURE INTO NEW SECTIONS.

The stamping in of the electrode mixture, warmed to 80° C. (176° F.) to make it soft, is done either by hand ramming or by compressed air hammers. An automatic machine can be used for

this work when the inner construction of the iron casing is not too complicated. When the stamping is finished the top surface of the mixture (which is left a little below the top edge of the iron casing) is covered over with some straw or bagging, in order to keep out dust and air and so keep it soft for the next mass stamped in to make good connection with it and stick fast to it.

In starting an entirely new electrode, it is built up of several sections in the manner indicated and the lowermost section is then baked by a moderate wood fire, piled around it. This solidifies the lower section so that the entire electrode can be lifted and put in place in the furnace, the holder adjusted and the current turned on. The electrode rests at first on some coke piled on the bottom of the furnace, and a small current is put on at first, rising gradually to full load.

The holder may be of any usual or effective design. That used on the 850 mm. electrode at Fiskaa is octagonal, having eight water-cooled contact pieces, each 80 cm. (32 inches) long (high) and made of brass. Clamps enable it to be screwed tightly in place; it can be moved when necessary, which may be only once or twice a week, with only a few minutes interruption of the current.

The addition of a new section of casing, including warming up the electrode mixture, stamping in the mass, and all other necessary work, require, in the 850 mm. electrode, about 30 man-hours labor per ton of electrode carbon. Six men, four feeding the mixture and operating the pneumatic stamping tools and two taking care of the warming operation and carrying mixture up to the platform, will stamp in one meter of 850 mm. electrode in four to five hours.

ADVANTAGES OF THE SÖDERBERG ELECTRODE.

Baked carbon taken from the furnace end of a Söderberg electrode is dense, hard, and of the ordinary quality of previously baked electrodes. It shows in this respect no difference from ordinary carbon electrodes. Laboratory tests at Fiskaa on such specimens have shown:

(a) Specific gravity about 1.5.

(b) Electrical resistivity (cold) 0.007 ohm per cm. cube.

(c) Crushing strength about 150 kg. per sq. cm. (2,140 lb. per sq. inch).

The Söderberg electrodes will certainly increase the regularity of running of electric furnaces to which they can be adapted, both because of their absolute continuity in respect to absence of joints and because of the uniformity of quality of the raw materials going into the electrodes, there being no such variation in the quality of these materials as is almost unavoidable when separate previously-baked electrodes purchased on the market are inserted one after the other.

The Söderberg electrodes, further, obviate the shutdowns which are necessary when built-up previously-baked electrodes are being changed or renewed, and this continuity of running is undoubtedly of great technical and still greater economic advantage.

Where the Söderberg electrodes can be used, they are certainly very much cheaper to use than ordinary previously-baked electrodes. How much cheaper will depend considerably on local conditions, cost of labor and supplies, and many other factors, but there is no doubt that the saving in running expenses will be sufficiently great to warrant the serious attention of everyone using furnace electrodes.

ELECTRODE CONSUMPTION.

In the period July 22-August 11, the electrode consumption at Fiskaa was taken during a regular run. No breakages took place in this period and in consequence no disturbances of the running occurred from this cause. As can be seen further from the table, the average electrode consumption, while producing 50 percent ferro-silicon, was about 53 kilograms per ton of 50 percent ferro-silicon. The furnace construction, however, caused a considerable phase displacement of the current (Cos. φ about 0.63) and considerable electric energy was also lost in the iron work around the furnace. For these reasons the above-given electrode consumption is considerably greater than it would have been if the electrical conditions were more favorable. The table also shows the electrode consumption per hour and per ampere-hour. Taking into account the poor electrical conditions and the furnace construction, the electrode consumption given may be regarded as good.

The table gives further the interruption of the current caused by stoppages for lifting the electrode holder. In the whole period there was used for this purpose 51.5 minutes, divided between six separate liftings of the holder and contacts. I saw the contact ring lifted at one operation about 30 centimeters, consuming four minutes, during which time the current was taken off the furnace. Usually it can be assumed that interruption of the current for this purpose is necessary every third to fourth day, and only for about five minutes each time.

VOLTAGE AND ENERGY LOSSES IN THE ELECTRODE.

Since the stamped but not burned electrode has poor electric as well as poor thermal conductivity, it is naturally of great importance to know at what place the baking of the mixture begins and ends. This was tested by using a sharp steel needle and introducing it through holes in the casing both below and above and immediately under the contact holder. The mixture above the contact ring was found to be somewhat soft, since the needle could be pushed in about 30 centimeters, a little above the middle of the holder it could be pushed in 10 centimeters, immediately below the contact plates the electrode was quite hard. It is therefore plain that with this type of water-cooled holder the baking of the electrode mixture takes place only to a limited extent above the contact ring.

The passage of current from the contact ring or holder to the electrode at the Fiskaa furnace, therefore, takes place principally from the lower part of the contact ring. In this connection the ribs of the iron casing must play a considerable part in the electrical conduction. Inside the contact ring the temperature is relatively low, and the conductivity of the casing iron therefore good, and this produces a better conductance of the electrode as a whole at this point. As a consequence of these conditions it is very probable that the iron casing of the electrode in the upper and relatively cooler part under the contact ring conducts the greater part of the current. The magnetic conditions produced in the iron casing will naturally generate a not-unimportant skin effect, and for this reason the effective conductance of the iron cross-section is decreased.

Ferro-Silicon Furnace, Using Söderberg Electrode.

Furnace type: Built for 1500 KW. with Scott connection *used* as a single-phase furnace with embedded bottom and top electrodes, taking on the average about 750 KW. with about 50 volts at the transformer terminals.

Dimensions of electrode: Diameter 85 cm. (34 inches). Cross section of carbon 5670 sq. cm. Cross section of iron 77.1 sq. cm.

July-August, 1919.

Operating periods	Operating time	Average of current in amperes	Current per sq. cm. of carbon section	Electrode Consumption				Kw. hour per ton 50% FeSi	Remarks
				per hr.	per 10,000 amp. hr.	per ton 50% FeSi	per 1,000 Kw. hr.		
From 20/7 to 28/7	175 hrs.	.....	....	2.57 kg.	....	50.7 kg.	4.1 kg.	12500	Altogether 30 minutes interruption of current while lifting electrode holder twice.
From 29/7 to 30/7	48 "	20000	3.54	2.71 "	1355	31.5 "	3.3 "	8470	No shifting of the holder.
From 31/7 to 3/8	93 "	18700	3.30	4.56 "	2420	49.5 "	5.7 "	8710	6½ minutes stop for lifting holder.
From 4/8 to 11/8	191 "	23100	4.07	4.21 "	1820	66.5 "	6.0 "	10900	Altogether 15 minutes stoppage for lifting holder 3 times.
From 20/7 to 11/8	507 "	.....	....	3.55 "	....	53.2 "	5.1 "	10500	

Approaching the working part of the furnace, the above relations are disturbed and modified. The warmer the electrode becomes the greater becomes the conductivity of the carbon, while the conductivity of the iron decreases. Where the electrode touches the charge, it is likely that the whole current passes through the carbon, particularly since the iron has almost all disappeared at this point.

In order to get data concerning the losses of voltage and energy in the electrode, measurements were made with the assistance of Engineer Lars Berg, on the electrode while in action, which are given in the annexed table.

MEASUREMENTS OF VOLTAGE DROP IN AND AROUND THE ELECTRODE HOLDER.

Diameter of electrode: 85 cm. (34 inches).
Cross section of carbon: 5,670 sq. cm.
Cross section of iron: 77.1 sq. cm.

Current load: 23,500 amp. equal to 4.15 amp./sq. cm. of carbon. In the table below, the first column gives the drop of voltage measured just before the holder was moved, distance from bottom of holder to top of charge being about 25 cm. (10 inches); second column gives the loss of voltage measured just after the holder had been raised 30 cm. (12 inches) corresponding distance above charge being about 55 cm. (about 22 inches).

Drop of Voltage.

Voltage Measured Between the Points Given:	Before Raising of Holder	After Raising of Holder
1. Holder to casing	1.2 volt	0.5 volt or less
2. Casing to carbon just below holder	0.75 "	0.6 "
3. Holder to carbon just below holder	2.2 "	1.3 "
4. Carbon to carbon 30 cm. apart (12 in.)	..	0.5 "
5. Holder to carbon about 35 cm. below holder	..	1.9 "
6. Copper bus-bar to carbon just below the holder	2.3 "	..
7. Ditto to carbon about 35 cm. (14 in.) below the holder	..	1.9 "

The specific resistance of the hot, baked electrode (carbon and iron) based on a drop of voltage of 0.5 volt between points 30 cm. (12 inches) apart, is equal to 0.00402 ohm per cm. cube.

Measurements were also made on the energy losses in the cooling water used on the electrode holder and contacts. The values found in such measurements are, however, dependent somewhat upon the radiation from the furnace and not alone upon the electric energy loss at the contacts. These observations are given in the appended table.

Heat Loss by Cooling Water.

Current load 23,500 amp.; Voltage 51 volts.

Distance from bottom of the holder to the top of the charge: In low position, 25 cm. (10 inches); in high position, 55 cm. (22 inches).

	In Low Position	In High Position
RIGHT HALF OF THE HOLDER.		
Temp. of outgoing water.....	35° and 33.8° C.	25° C.
" " ingoing "	14.0° C.	14° C.
Difference of temp.....	20.4° C.	11° C.
Amount of water in 2 min.....	54.1 kg.	53.3 kg.
Calories (kg. cal.) per sec.....	9.20	4.88
Equivalent KW.....	38.33	30.33
LEFT HALF OF THE HOLDER.		
Temp. of outgoing water.....	31.0° and 33.50° C.	24.5° C.
" " ingoing "	14.0° C.	14.0° C.
Difference of temp.....	17.25° C.	10.5° C.
Amount of water in 2 min.....	58.30 kg.	51.8 kg.
Calories per sec.....	8.04	5.05
Equivalent KW.....	33.50	21.04
Total KW. consumption	71.83	51.37

From the two last tables it can be seen that the electrical and thermal conditions vary somewhat with the position of the electrode holder. This is particularly true of the contact resistance between the contact pieces and the iron casing of the electrode. In this connection we can assume that the conditions might be considerably improved both in regard to diminution of voltage losses and of heat losses in the cooling water.

USES OF THE SÖDERBERG ELECTRODE.

The electrode in use at Fiskaa had been in continuous work since July 22d, a little over three weeks. The electrode was used in a single-phase furnace of common type, with bottom electrode, and was employed in making 50 percent ferro-silicon alloy.

The power-house conditions did not permit a greater voltage on the low-tension side of the transformer than about 50 volts, on account of the high amperage which was necessary in order to thoroughly test the electrode. Because of these electrical conditions the electrode had to work quite deep in the charge, and consequently a greater consumption of electrode was recorded than would have been necessary under more favorable electrical conditions. The consumption of carbon electrode during the above period (not including the iron of the casing) was 53 kilograms per ton of ferro-silicon alloy produced.

The electrode worked in all respects fully satisfactorily and no annoyance or trouble was experienced from tar vapors, which are expelled very slowly by reason of the very slow baking of the electrode. The baking takes place continuously and slowly at about the region or zone of the upper part of the contact with the holder, not on a horizontal plane across the electrode but at a higher point in the middle of the electrode than near to the outside surface. The contacts of the holder are moved up a suitable distance every third or fourth day during normal working; after each such movement upwards of the contacts tar gases appear below the holder contacts and burn gently for some three or four hours.

The use of the Söderberg continuous electrode will undoubtedly show advantages in furnaces of this construction, *i. e.*, in open or partly closed furnaces such as are at present used for the production of various ferro-alloys, calcium carbide, and similar products. Especially will this be the case where it replaces built-up electrodes with contacts for conductors placed on the upper end.

Electrodes of still greater size than the 850 mm. (34-inch) electrode in use at Fiskaa can undoubtedly be made and operated, which will be of particular advantage when replacing the largest sizes of built-up electrodes, with consequent saving in electrode material, labor, time and expense.

In closed furnaces with vertical electrodes, and where these are not exposed to any considerable lateral pressure from the charge, the use of the Söderberg continuous electrode may be also of great advantage. In this class of furnaces can be included most of the electric steel furnaces at present in use.

In furnaces where the electrodes pass through an arch into a closed melting chamber in a position more or less inclined to the vertical, and are exposed to lateral pressure from the charge, the use of such self-baking continuous electrodes may be possible, but will require the making of practical tests to adjust them to meet these requirements.

The above observations and data obtained at the Fiskaa works of the Norske Aktieselskab for Elektrokemisk Industri, were accumulated with the co-operation of Prof. P. Farup, formerly Professor of Chemistry at the Technical High School in Trondhjem, Norway, and Mr. E. Nystrom, engineer in charge of the electric pig iron smelting furnaces at Trollhattan, Sweden. I wish to acknowledge here the important part which these gentlemen took in gathering the above information, which was incorporated into a report to the A. S. Elektrokemisk Industri; also to thank the latter firm for permission to publish this description. From the interest already manifested by European electrochemical firms in the Söderberg electrode, it appears certain to the writer that there will be a rapid and profitable introduction of the electrode into many European electric furnace plants, and undoubtedly America will not be backward in utilizing the advantages of this invention.

DISCUSSION.

J. W. RICHARDS: Three 32-inch electrodes are being installed on a ferro-manganese furnace at the plant of the Southern Manganese Corporation, at Anniston, Alabama. There has been difficulty in getting supplies and material for construction, but it is expected that the furnace will be in operation next month. When in operation, the arrangement with the Southern Manganese Corporation is to the effect that anyone who is interested in seeing

the electrode in operation in order that they may assure themselves of its practicability, may visit this works. The Hart Trading Company, Tribune Building, New York, is in responsible charge of the business arrangements on this side of the ocean.

S. A. TUCKER[1]: With reference to Mr. Swan taking this up, I do not know whether it is good or bad, but I do know something about Mr. Swan, because we had a good many dealings with him, and he is one of the most enterprising men, I believe, that we have got in the country. I would like to ask Prof. Richards what the specific resistance of this electrode is compared to some of the others?

J. W. RICHARDS: Specimens of the baked part, from the holder down, show identical resistance with ordinary well-baked carbon electrode. The upper part of the electrode is soft and therefore practically non-conducting, so the holder must be placed down upon the baked part unless the casing is made strong enough or heavy enough to carry the current. In a small electrode, it is practicable to make the casing heavy enough to put the holder wherever you please, but in the larger electrodes it is run close to the furnace.

COLIN G. FINK[2]: I do not believe Dr. Richards brought out emphatically enough one of the advantages of this unbaked electrode, and that is the elimination of transportation, which is very difficult and costly with some of the two-foot diameter electrodes. Furthermore, the care of the large electrodes is a very important matter. Ordinarily the electrode occupies the best place in the foundry, a warm, dry and protected place. If an electrode is not kept perfectly dry, you run into spalling difficulties, and if any part of the foundry is exposed to moisture and frost, the spalling will be excessive. Spalling is reduced to a minimum through the introduction of this continuous electrode.

L. E. SAUNDERS[3]: In the description of the ingenious arrangement for keeping the smoke away from the workmen who are making the casing, it is not stated how the smoke is kept from the rest of the building, and I wonder if that is not a serious

[1] The Chemical Foundation, Inc., New York City.
[2] Head of Laboratories, Chile Exploration Co., New York City.
[3] The Norton Co., Worcester, Mass.

matter in some sorts of industries? Further, I would like to ask how they would manage in case the iron of the casing would contaminate the product which was being melted in the furnace?

J. W. RICHARDS: The baking is so slow that practically there is no smoke in the building. I was prepared to see a good deal of smoke around the electrode, but there is hardly any more than you see when using an ordinary electrode. I asked myself "where has the smoke gone to?" and the only answer I could suggest was "it cannot get out above and it is therefore practically forced down into the furnace through the baked part, where it decomposes and deposits carbon on the red hot part of the electrode." When the holder was raised, however, for a short time there were a few evidences of yellow smoke coming out under the holder, because the outer part of the electrode underneath the water-cooled holder had apparently not been baked as thoroughly as that which was inside. When the holder was raised there was a little escape of yellow flame perhaps six or eight inches high around the electrode for a short time, but it was entirely negligible as far as the plant was concerned. Practically you can say that the smoke or the distillation products are not in evidence at all. The burning is done very slowly, in general, I take it, at the rate of about one meter a week. It is done much more slowly than the ordinary burning of electrodes, and the gas is continuously forced down into the furnace.

L. E. SAUNDERS: In other words, you change the smoke into electrode?

J. W. RICHARDS: Practically that. If iron is not desired in the furnace, what is to be done with the casing? So far it has been used in ferro-alloy furnaces, in which case the iron of the casing does not count. If used in a calcium carbide furnace, I think it has been calculated that the amount of iron present as casing would represent about two-tenths of one percent in the product, or only a fraction as much as is obtained from the ash of the materials used. If the electrode were to be used in other furnaces where iron was not desired, then some other means of keeping the electrode encased would be necessary. For instance, if it were used in aluminium pots, it is likely the electrode might be encased in sheet aluminium. This problem is quite attractive,

because at the present time it is in process of being developed. Several other applications are not yet thoroughly worked out.

ROBERT TURNBULL[4] (*Communicated*): The Söderberg electrode appears to be an attempted improvement of the old system of building a carbon paste around a graphite electrode, which was partially baked, and the final baking allowed to take place when the electrode was put in the electrode holder of the furnace.

Under present-day improved methods of operating where shutdowns on large furnaces are practically nil, a new electrode being added in less than ten minutes' time, the many delays which one could not possibly avoid by the use of the Söderberg system, would entail serious curtailment in the output of the furnace, which in the case of ferro-silicon, at the present low selling price, would create an impossible situation.

The automatic baking out of the electrode claimed by the Söderberg inventors would only be possible when sufficient heat is generated in the electrode itself to do this baking. In some furnaces where very large electrodes are used, and small densities of current, where they do not heat up to any great extent, this baking would not be accomplished.

When the round paste which forms an electrode is put in place, owing to the presence of tar and pitch in the mixture, this paste becomes very hard, and when heat is applied to it, it becomes very soft, and does not harden again until the volatile gases have been expelled. There is a doubt in my mind as to whether sufficient hardening of the electrode will have taken place before it reaches the electrode holder, and if this is so it would immediately go to pieces when slipped through the holder.

The addition of the paste in the steel receiver above the furnace seems to me to be impractical, as the men doing this work would be exposed to the gases of the furnace when this operation is being accomplished, and although the furnace might be shut down for a few minutes to allow for this operation being performed, there would still be enough gases from the other furnaces alongside to prevent the workmen from working at their ease, and in safety. This inconvenience is not incurred when adding a new electrode under present working conditions, as the electrode is added below the gas level.

[4] Managing Director, U. S. Ferro-Alloys Corporation, Niagara Falls, N. Y.

The cranes and self-charging system used in the operation of electric furnaces today would also be seriously hampered by the application of the Söderberg electrode. In fact, I do not see how both could be utilized.

I would like to ask this question. Certain results in kilowatt-hours utilized in the production of one ton of ferro-silicon are given in Professor Richards' paper, where the Söderberg system was used. The kilowatt-hours given are 11,000 per ton. Am I to understand that this amount of power was used in the production of one ton of ferro-silicon? If so, would I be right in assuming that 5,000 kilowatt-hours are used per ton of ferro-silicon to bake the Söderberg electrode? The average consumption of electric power in the United States is 6,000 kilowatts to perform the same work with the standard American manufactured electrodes.

J. W. RICHARDS (*Communicated*): Replying to Mr. Turnbull's remarks, the system of the Söderberg electrode involves a great deal more than building up carbon paste around a graphite electrode core; for instance, the casing is one essential item of difference, and there are many others. In practice, it will be found that the interruptions using the Söderberg electrode are only a fraction as long or as many as using ordinary carbons. The electrode is not baked by the heat generated in the electrode itself, as Mr. Turnbull thinks, but mostly by the heat conducted up from and radiated from the furnace itself. The electrode does not go to pieces when slipped through the holder, because it is slipped only a few inches at a time, but it may be assumed that if it were suddenly slipped a foot or two that there might be danger of the lower baked part separating from the upper unbaked part. That has happened once to the Norwegian furnace, in the early experimental stage, but has not happened in several months' practical running. The liability to this mishap is negligible at present.

The job of welding on the new section and ramming in the paste is done in a small, ventilated, gas-tight booth, into which the furnace gases do not enter at all. The men working at that task are more comfortable than those working around the furnace shoveling charge. The cranes must be allowed for, and the tamping booth kept below their working level. The power required to bake the Söderberg electrode is really for the greater

part waste heat which would pass up any electrode and be lost anyhow. Its amount will be found nearly negligible or inappreciable in regular practice. The reason so much power was used per ton of product on this Norwegian furnace was principally because it was only running at about half its normal capacity, and more power could be had from the electrical supply. The power consumption on a normally operated and designed furnace, using Söderberg electrodes, is sure to be no greater than normal, and perhaps less; I feel sure of that.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

SYNTHETIC ELECTRIC FURNACE CAST IRON.[1]

By Ch. A. Keller.[2]

Abstract.

A description of the great development in France, during the war, of electric furnace processes for converting steel turnings from munition plants into low-carbon cast iron, high in silicon and low in sulphur and phosphorus, for the production of cast-iron shells. Several types of furnaces were used, and the method was varied according as to whether very low sulphur or very low phosphorus, or both, were desired. One large plant was put up near Paris to utilize power from the Paris power plants; others were developments in and near Livet, at the works of the Keller-Leleux Co.

I. Introduction.

The subject of this paper is the manufacture of pig iron in electric furnaces by recarburizing fusion of steel turnings or scrap. These materials are melted in presence of carbon in an electric furnace, producing thus synthetic cast iron.

The fact that steel can be carburized to cast iron is no novelty, but has been known for a century or more. This process was limited however to the carburization of low carbon steel to high carbon steel, and was never regarded as a method of obtaining cast iron, either practically or economically.

The author patented[3] in 1908 and 1913 the fusion of steel turnings mixed with carbon as a continuous method.

[1] Manuscript received Sept. 1, 1919; translated by J. W. Richards.

[2] Managing Director of Keller and Leleux, 3 Rue Vignon, Paris, France.

[3] French Patent C. A. Keller 405277, 10 Nov. 1908; certificate of addition No. 19358, 11 Sept. 1913.

It is easily understood that the fusion of steel turnings charged cold in a covered furnace would need an amount of heat energy corresponding to the fusion temperature of steel; the thermal efficiency of a furnace working at such a high temperature is much lower than that of a furnace working at the fusion point of cast iron. This is especially true if the steel furnace is of the ordinary reverberatory type, while the fusion of cast iron can be accomplished in a different type of furnace. A vaulted roofed furnace is moreover not very convenient for the charging of turnings or scrap. The carburizing of melted steel turnings can only be done

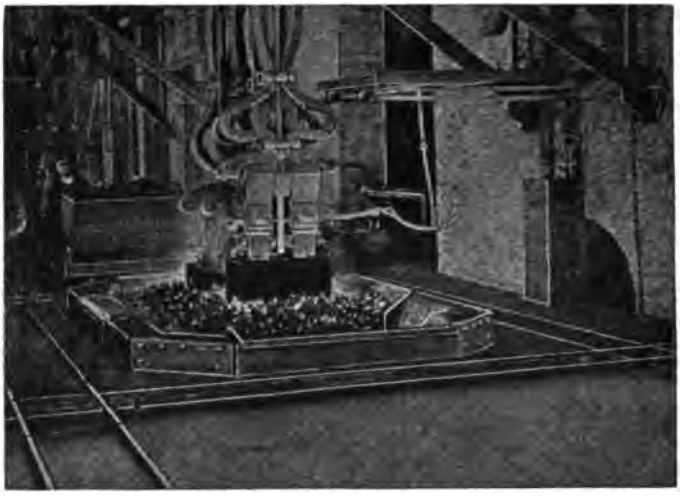


FIG. 2. Keller Furnace working continuously on synthetic pig iron.

by dissolving the carburizing material in the upper layer of the bath. This solution becomes slower the higher the content of carbon becomes. Further, if the furnace, as is usual, is emptied after each charge, there is considerable loss of heat in this intermittent operation, especially while repairs to the hearth and roof are being made. When mixtures of turnings and carbon are melted down in a shaft furnace, the carburizing proceeds much quicker because of the intermixture of the steel with the carbon; the carburizing actually begins far below the melting point of the steel, even at a bright red heat in the upper parts of the charge, and accelerates as the charge becomes hotter as it descends in the

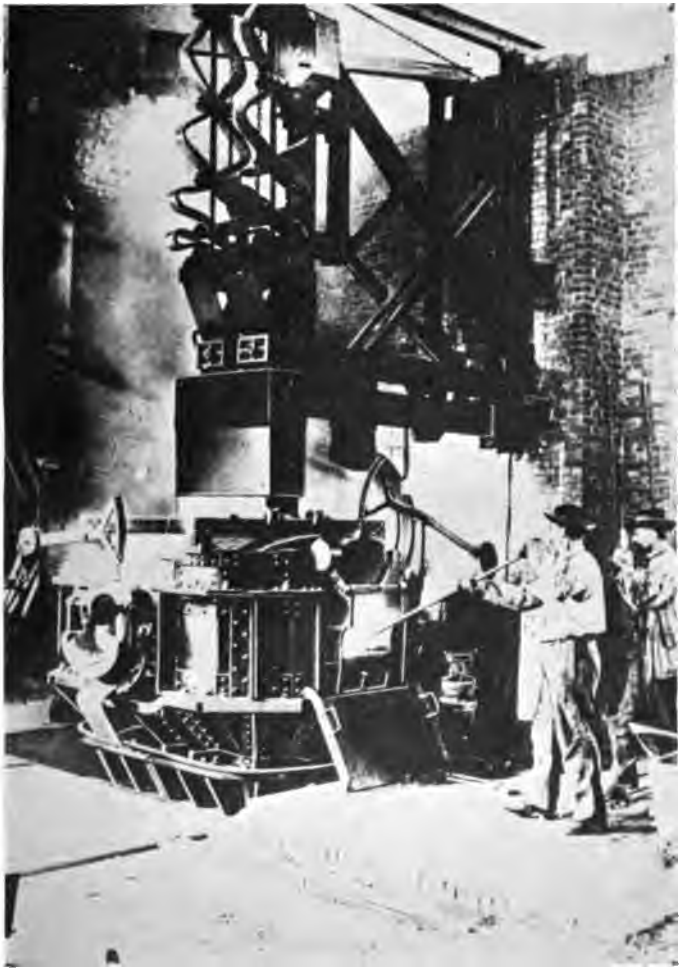


FIG. 1. Keller Furnace working discontinuously, carburizing liquid steel.

furnace. There is thus a carburizing of the iron produced by contact of the solid carbon with partially carburized metal, about to be fused; in this manner the cast iron is actually formed, melted and run out of the furnace at temperatures of 1200° to 1300° C.

I have thus far spoken of the carburizing of the metal. However, the proper working of an electric furnace for melting such a charge depends also on other considerations. The mixture of steel turnings and carbon is a very good conductor; it would be therefore necessary to run the electric furnace with a voltage so low that it would require impracticable amperage. Besides this it would be regrettable to use electric fusion without profiting

FIG. 3. Works at Livet. Handling of castings by electric crane and magneto hoist.

from the metallurgical conditions which permit of desulphurization. The latter is accomplished by use of a basic slag whose ingredients should be part of the charge, and thus accomplish, in parallel, desulphurization with carburization. These slag-forming ingredients will also have the further influence of diminishing the electric conductance of the charge, and thus render the electrical operation of the furnace easier, besides completely desulphurizing the product.

The process as just described may be summarized metallurgically as obtaining cast iron in the presence of a sufficient basic slag, conserving the silicon in the charge but eliminating its sulphur, thus utilizing the carbon charged solely for carburization, without any reduction of silicon from silica. By this method,

white cast iron may be easily obtained from ordinary commercial steel turnings and scrap. For example, the following results have been obtained:

Steel Turnings		White Cast Iron	
Silicon	0.44	Silicon	0.52
Manganese	0.55	Manganese	0.48
Sulphur	0.07	Sulphur	trace
		Carbon	3.55

The composition of the cast iron may however be varied if desired. The introduction of a certain quantity of silica into the charge will increase the silicon in the product, with a corres-

FIG. 4. Works at Livet. Foundry for projectiles of large calibre and high strength.

pondent reduction of the amount of carbon therein. The content of silica in the slag will vary inversely as the quantity of silicon in the cast iron.

It results from the above that the calculation of the charge and its proper adjustment permits the obtaining of any desired composition of pig iron. I have run an electric furnace producing 80 to 100 tons of cast iron per day without greater variations in a month's running than 0.25 percent in the carbon and the silicon in the product. For such close running, the composition of the slag must be closely controlled, and the quantity of carbon in the

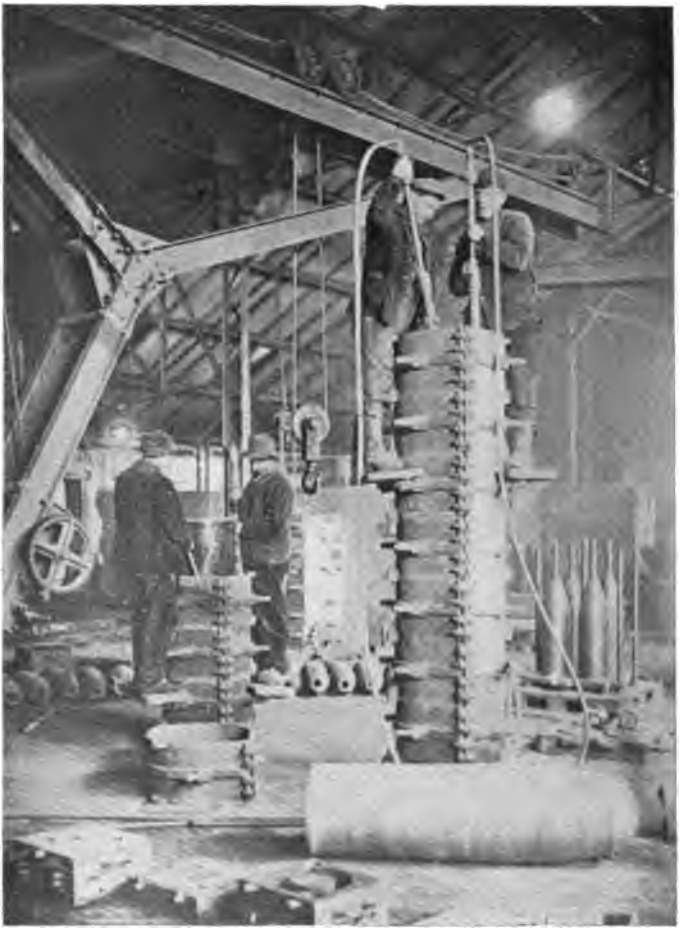


FIG. 5. Works at Livet. Projectile Foundry.

charge must be exactly adjusted. The process may be thus made very precise, but depending absolutely upon the co-operation of the works laboratory for its success.

The carburizing carbon should be used in a state of division corresponding to that of the steel turnings, so as to assure intimate contact. Ordinary coke answers well, also wood charcoal; either one or the other is used according to their price and the purity of the product desired. Previous drying of the coke is necessary, in modern efficient dryers.

The process thus described runs very simply, without any spe-

FIG. 6. Tilting Keller Furnace: Metallic casing and conducting hearth grid.

cially trained workmen, because all the results depend on the proper preparation of the charge, and thus rest entirely on the proper analyses and calculations of the chemist and metallurgist.

With a properly constructed furnace, the upper part of the charge is heated by the gases produced lower in the furnace, and in a furnace of 2500 kw., producing 80 to 100 tons per day, we have reduced the power consumption to 675 kw. per ton of cast iron. Further, the furnaces are very little corroded by such a charge. One of the above furnaces, at Livet, worked six months with no repairs to the lining, casing or other parts; it was put out of action by lack of power due to low water.

It is not necessary to dilate further upon the fundamental differences between the slow carburizing of melted steel by dissolving carbon in a bath of steel and the obtaining of cast iron by the method just described. The metallurgical as well as the economical differences in the two methods are striking and considerable.

Working as above described, we obtained in regular running the following results:

The consumption of electrodes, when of good quality, was reduced to 6 kg. per ton.

The consumption of steel turnings, non-oxidized and free from rust, was 1050 kg. per ton of cast iron; this figure may exceed 1100 kg. with ordinary rusted or oxidized turnings.

FIG. 7. 400 mm. Shells "in the rough."

The quantity of coke, carrying 80 percent fixed carbon, required to produce a ton of cast iron, containing 3 percent carbon and 1.75 percent silicon, from ordinary projectile steel scrap, is about 80 kg.

An 80 to 100 ton furnace, furnished with proper devices for mechanical charging and operation, requires not more than fifteen men for preparing the charges, charging and operating the furnace. Casting and charging the product into cars requires seven men; stacking in the stock yard, two men.

If these synthetic cast irons have found a large field of appli-

FIG. 8. Works at Livet. Capping Shells.

Fig. 9. Works at Livet. Pouring from the Electric Furnace.

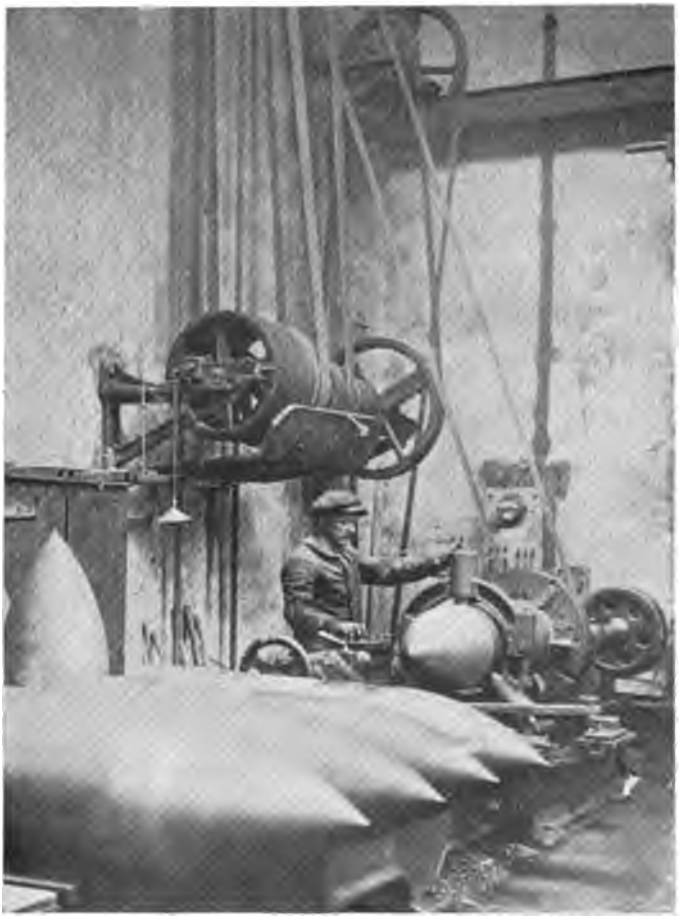


FIG. 10. Works at Livet. Machining Castings.

Fig. 11. Hydro-Electric Power Plant des Vernes á Livet.

cation during the war, because of the great production of steel turnings in the projectile factories, they have however a place in industry after the war, for example in producing castings of extra mechanical strength.

It is natural to place a foundry alongside of the furnaces producing these synthetic cast irons, as is done at our works at Livet. In such a case the cast iron from the furnaces producing it is most conveniently assembled in a reservoir or mixer, from which the foundry takes out such quantities as it needs, and when

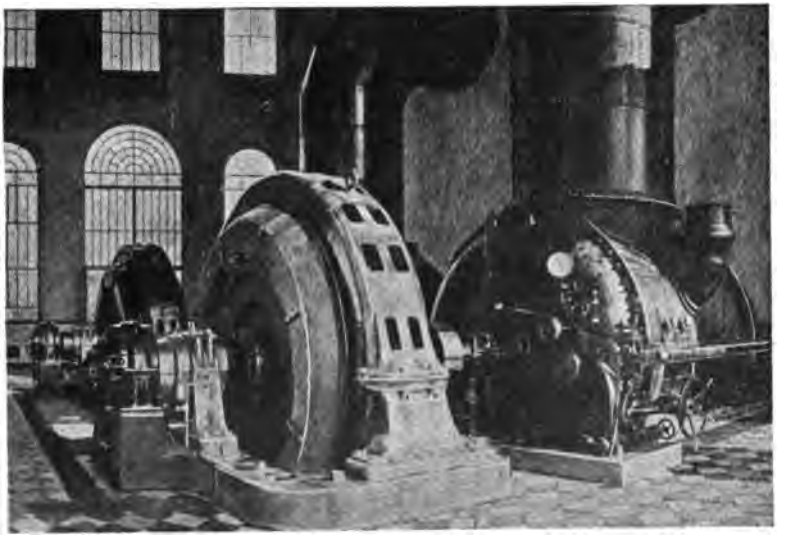


FIG. 12. Works at Vernes: 3,500 H. P. Turbine and Generator.

needed, for casting. Such a mixer permits of specimens being taken and analyses being made of the metal before it is used in the foundry, in order to assure proper quality in the castings.

It is likewise possible to manufacture cast iron intended for "malleable" castings, that is castings to be put through the malleablizing process, since the low silicon and manganese in the steel turnings, and the restraining of the carbon in the product, allow the production of this quality of cast iron. Other special qualities of cast iron, such as those containing nickel, chromium, titanium, etc., can be likewise manufactured. The absence of hydrogen,

nitrogen, carbon-monoxide and dissolved air make the synthetic cast iron particularly valuable for these special alloys.

The metallurgical conduct of the process needs to be considerably changed if dephosphorization must be attained in the process; this I have accomplished by a double operation. First, the steel turnings are melted in presence of a small quantity of carbon and a basic oxidizing slag. The carburization is made as high as

FIG. 13. Panoramic View of the Utilization of the Falls at Baton.

possible consistent with the proper running of the furnace and dephosphorization of the charge. Keeping the carbon at one percent or slightly higher we accomplished this result. The dephosphorized metal thus obtained, low in silicon and manganese, is cast into small ingots which are then remelted in admixture with the necessary carbon and the ingredients for a desulphurizing slag, the latter being chosen particularly low in phosphorus.

This double process increases somewhat the cost of manufacture; the power absorbed is about 750 kw. hours per ton of product

of the two operations. The extra costs are balanced by the extreme purity as regards phosphorus, as well as low sulphur, and its accurate content of silica and manganese. From a commercial standpoint it can compete with Swedish cast iron.

I will close this brief review of the principal metallurgical results obtained by indicating a variation of the product for the manufacture of steel, starting with steel turnings.[4]

In this process the steel turnings are melted in an open furnace as in the previous case, but with a slag which is not oxidizing or

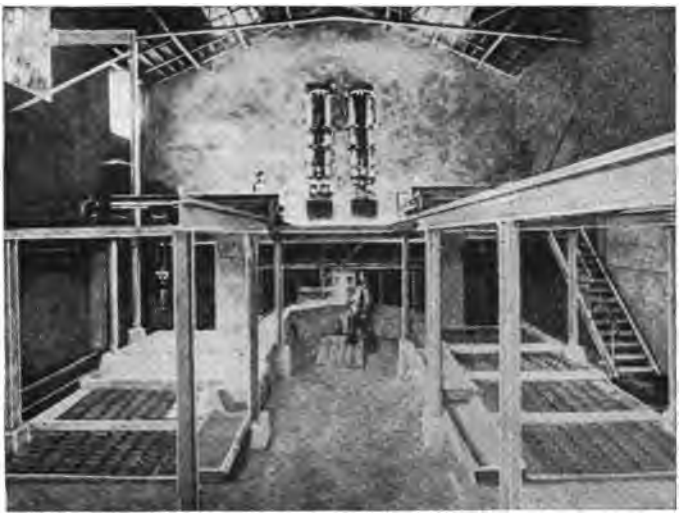


FIG. 14. Works at Limoges: Furnace and Casting Beds.

desulphurizing, and the quantity of carbon put into the charge is only sufficient to reduce the oxide on the turnings and to carburize the metal to a little above the carbon content required in the steel. This facilitates the transfer of the desulphurized metal and permits the use, in a second operation, of an oxidizing process. For example, if one wishes a steel with 0.5 carbon, the metal of the first melting furnace will be cast with 1.5 carbon, and will have been deprived of sulphur during the fusion; the furnace may be either an open-hearth or an electric furnace which is worked oxidizingly so as to reduce the carbon to the desired

[4] French Patent, C. A. Keller 80928, 29 December, 1915.

percentage and at the same time dephosphorize the metal, as in ordinary steel practice.

By the above described processes, the production of synthetic cast iron by the Keller-Leleux Company, at its works at Livet, Nanterre and Limoges, has amounted during the war to over 150,000 tons. The description of these works and their operation forms the second part of this paper.

II. Industrial Exploitation.

1. *Works at Livet.*

In 1908 I commenced at these works the study of "extra strong steely cast iron" obtained directly by the carburizing of steel turnings in an electric furnace.

Later we proposed to build a plant for the manufacture of "malleable" cast iron, but this enterprise was interrupted by the war. When the specifications appeared for projectiles of low-carbon cast iron, at the beginning of the war, I took up at once the question of manufacturing this variety of cast iron with the properties prescribed by the Department of Artillery. By November, 1914, I had attained my object and produced cast iron of the following analysis:

Carbon	2.90
Silicon	1.75
Manganese	0.50
Sulphur	trace
Phosphorus	0.05

Mechanical tests of this material showed: tensile strength up to 50 kg. per sq. mm. (71,000 lb. per sq. in.); resistance to shock, up to 60 blows of a weight of 12 kg. falling 89 cm. on a test piece 40 mm. square, by 40 cm., resting on two knife edges 16 cm. apart, the height of the fall increasing one cm. at a time until rupture occurs. The Artillery specifications call for a minimum of 25 kg. per sq. mm. (36,000 lb. per sq. in.) tensile strength and at least 18 blows of the weight falling 44 cm.

A 2-ton electric furnace was put at work in manufacturing these projectiles in 1914. The regularity of the metal and the tests obtained from it were so favorable that before the end of 1914 a series of shells 220 mm. in diameter had been made and were

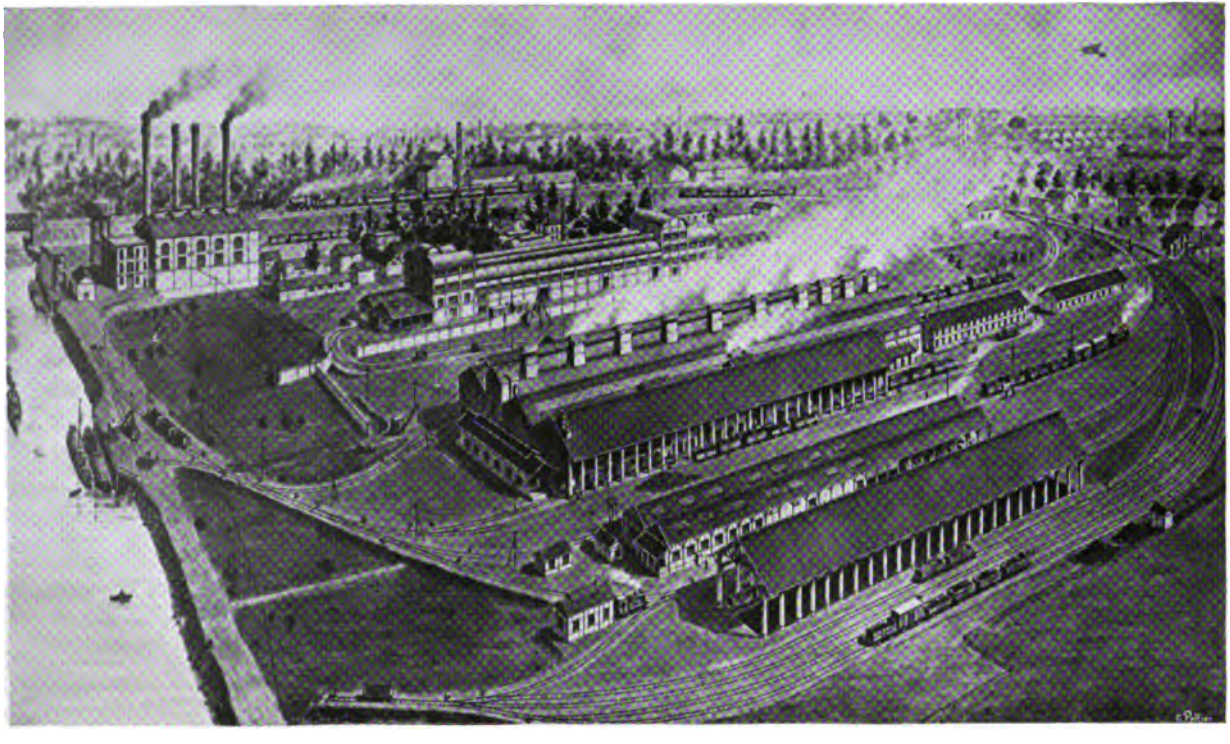


FIG. 16. National Artillery Foundry at Nanterre.

tested at the Bourges testing ground. Arrangements were at once made with the Artillery Department for the manufacture of 220 mm. shells, which was begun at Livet in the beginning of 1915, and eventually a complete foundry was erected alongside of the electric furnace plant for manufacturing the cast iron. Its production was at first 50 projectiles per day, which was increased in 1916 to 300 projectiles of 220 mm. and 10 shells of 400 mm. diameter, representing altogether 55,000 kg. of casting metal required.

To get the most uniform quality of metal for the foundry, the metal obtained in the three manufacturing furnaces was trans-

FIG. 15. General View of the Works at Villefranche de Conflent.

ferred into three electric mixing furnaces of seven tons capacity each, run by 400 kw., to keep it hot and melted for the use of the foundry and for the control of its quality. The analysis for carbon, taking 20 minutes, was made on a test taken from these mixers just before casting. These electric mixing furnaces are of the Keller electric steel furnace type, with roof and side doors for working. The electric current enters by a vertical electrode and is taken off by a grid rammed into the hearth, as shown in Fig. 6. Repairs are made with a mixture of magnesia and fragments of iron agglomerated with tar, corresponding in principle with open-hearth steel furnace practice.

The liquid cast iron is covered with basic slag as a protecting layer against oxidation and the super-heat of the electric arc. When pouring, this layer is easily kept back by a dam of bricks.

Practice has shown the usefulness of these electric mixing furnaces, which hold the metal so that its composition can be closely controlled. In general, the metal stays about one hour in the mixer, if the filling of these furnaces is well timed with the molding practice in the foundry. If the composition is not as exact as desired it can be easily modified in the mixing furnaces. The maintenance of these mixers is easy, their service being very light; the hearths last about two months and the roof more than

FIG. 17. Electric Furnace House for Synthetic Pig Iron.

three months. The consumption of electrodes in them is about 2 kg. per ton of cast iron, and the electric energy 50 to 100 kw. hours per ton. A single workman controls a mixing furnace, operates the pouring and takes the specimens.

The machining of the shells was at first done by sub-contractors, but was transferred to a plant erected in Livet towards the end of 1916, thus saving time, transportation and extra handling. Besides, the turnings obtained from the machine shops were immediately utilized in the electric furnaces. The scrap produced was thus reduced to a very small quantity, finally reaching only 7 per-cent on the weight of the cast shells.

FIG. 19. National Artillery Foundry at Nanterre.
(First three furnaces producing calcium carbide for cyanamide manufacture, the further furnaces on synthetic pig iron.)

The production of the cast iron at Livet commenced on a scale of 20 tons per day, was soon increased to 60 tons, and finally to 300 tons daily during periods of high water when sufficient power was available. Several other outside machine shops were supplied with this cast iron besides our own shops at Livet.

The quality of cast iron furnished to outsiders was fixed as carbon approximately 2.75, silicon approximately 2 percent. When such metal was melted in a cupola the specifications required by the Department of Artillery were usually obtained, without the further addition of steel, because of the slight recarburization and oxidation of silicon occurring in the cupola. The shipments to such outside foundries were accompanied by the analyses, and

FIG. 18. Storage Bins for Turnings (left) and for Coke (right).

an indication of the quantity of steel or ferro-silicon to be added when it was necessary. This practice assisted greatly in obtaining uniform metallurgical results in the projectile foundries.

The capacity of the plant at Livet finally became insufficient and a new plant was undertaken in November, 1915, which was put in operation 12th of July, 1916, at first with a furnace capacity of 80 to 100 tons per day and subsequently enlarged.

The buildings consisted of four parallel shops, the first 300 meters long for the reception of raw material, particularly that of steel turnings which was handled by an electro-magnet suspended from an electric traveling crane. The second shop was for the preparation of the charge which was then raised to the level of the furnace floors in the third shop.

The third shop contained 5 Keller furnaces in a row, four of

2000 kw. and one of 2500 kw. The capacity of this plant is 300 tons of synthetic cast iron per day. The grids of cast iron from the casting beds in front of the furnaces are removed by an electro-magnet hanging from a traveling crane which serves the four furnaces. The cast iron bars thus produced were shipped to outside foundries. If liquid cast iron for the mixing furnaces was desired from these furnaces, they were tapped on the opposite side into ladles, which were then taken to the mixers.

The new plant comprised further two large shops for rolling mills and accessory operations.

FIG. 20. Charge Mixing House and Transformer Enclosures.

2. *Installation at Vernes.*

The rapid increase of the works at Livet required increased hydro-electric power. 7000 h. p. was thus harnessed at the water-fall of Vernes on the Romanche. This new power plant was begun in August, 1917, and started in operation July, 1918, in time to be of some service before the finish of the war. The head was 20.5 meters (61 ft.); the nominal power 7000 h. p.; the hydraulic works comprised a canal under the Livet works 208 meters long, a tunnel in the mountain 15 sq. meters section and 620 meters long, and an open conduit of reinforced concrete 3.6

meters in diameter. Two steel tubes 2.5 meters in diameter fed the two 3500 h. p. turbines.

This amount of power corresponded to an increase of production of synthetic cast iron of 25,000 tons per year.

4. *Hydro-electric Plant at Baton.*

In order to increase still further the power disposable at Livet, the firm of Keller and Leleux undertook, towards the end of 1917, to develop the fall at Baton which has 1100 meters head. The completion of this work is expected towards the end of 1919, the

FIG. 21. Wagon Track for Charging Buggies.

tunnel 1050 meters long, situated at an altitude of 1900 meters, being not yet finished. When finished this development will add 7000 h. p. to the resources of the company.

4. *The Plant at Limoges.*

Working in parallel with the installations at Livet, the Keller-Leleux Company erected at l'Aurence, near Limoges, a small plant to utilize the surplus power of the hydro-electric plant of Eymoutiers. The electric furnace installed had a capacity of 1000 kw. and has worked in parallel with the tramway circuit since 1916, and demonstrated the practicable possibility of such an arrangement.

5. *Plant at Villefranche.*

An installation of the same general provisional type, of 2000 kw. capacity, was erected by our company at Villefranche de Conflent (P. O.), to utilize the surplus electric power of the company "du Midi" on its railroad Perpignan-Bourg Madame. This installation, which has just been completed, is now in charge of the "Société des Fontes Synthetiques du Midi," *procédés* Ch. A. Keller.

FIG. 22. **Casting Beds for Synthetic Pig Iron.**

6. *National Artillery Foundry at Nanterre.*

About the close of 1916, Mr. Albert Thomas, Under-Secretary of State for Artillery and Mr. Claveille, Director of Artillery Manufacture, entrusted me with studying out and erecting for the state, at Nanterre, a works to manufacture 300 tons of synthetic cast iron per day, intended to utilize the electric energy of the Paris power plants.

The electrometallurgical plant thus erected was called "The National Foundry for Artillery at Nanterre." It contained seven furnaces, of which six were to be in continuous operation, and absorbed 10,000 kw. It was constructed in 182 working days, with the energetic co-operation of the General Company for Civil Enterprises. It was put in operation the third of July, 1917. It

was successful from the start, and the product was highly esteemed by the foundries using it. In the furnaces of 1650 kw. type used, the following results were obtained per thousand kg. of product:

Steel turnings used	1133 Kg.
Coke	89-95 "
Electrodes	6-10 "
K. W. Hrs. consumed	815

The arrangement of plant was in principle the same as that at Livet. The bins for turnings and coke are shown in the cuts on page 201. They were operated by means of clam shell buckets from over-head traveling cranes. The coke was crushed to size and then dried in a rotating dryer to 1 percent moisture or less. The mixing room was close to the stock room.

The regulating of the electrodes of the furnaces is effected by hand, the variations of furnace conditions being very small.

The installation at Nanterre comprised a shop for preparing and assembling the electrodes. They are built into blocks of four.

An exterior stock-shed for turnings was provided, 150 meters long, capable of stocking 50,000 tons.

The installation was completed by a building containing offices, laboratory and hospital quarters.

The labor was largely performed by prisoners of war.

In view of the urgency of war requirements, the works at Nanterre has been increased to 15,000 kw. utilizing 10 monophase furnaces of 1650 kw. each, installed in a shop 175 meters long.

III. Conclusion.

The war has certainly given to synthetic cast irons a very rapid development, particularly based on the great abundance of steel turnings. Up to 1916 large quantities of these turnings were exported, particularly to Italy and Spain. Also blast furnaces consumed considerable quantities, and there was later competition between the blast furnace and the electric furnace for this material. The question of transporting these materials to the furnaces played a considerable part in the question of their destination and utilization.

However, it is a fair question to consider if the recarburizing fusion by electrical energy developed by water power is not the

best utilization of this material in an absolute sense, because it entails saving of fuel. We believe that these steel turnings ought to be treated in electric furnaces operated by "la Houille Blanche."

These considerations may be changed after the war is ended. The possibility of the manufacture of synthetic cast irons which are not dephosphorized will depend on the market for steel turnings, and also on the price of coal relative to that of electric energy. All these relations should be the subject of close study. I believe however that electrically produced synthetic cast iron has occupied an honorable place in the service of National Defense, whatever may be its future development.

DISCUSSION.

F. W. BROOKE[1]: There is one point I have often noticed in making synthetic cast iron, and that is, especially using steel turnings, the trouble experienced in getting the high carbon content. Obtaining a low sulphur and phosphorus content is one of the main objects of this process, but every now and again one has to meet specifications where high carbon content is required; my own experience has been that it is quite easy to obtain 2.75 of carbon, but to get 3.75 is one of the great difficulties, especially in a furnace where a roof is used. Getting that last half or quarter percent of carbon is a very serious difficulty as regards the effect on the life of the roof, and I wonder whether anyone present here has had that same difficulty?

J. W. RICHARDS[2]: The paper makes the statement that they have no difficulty in producing pig iron with three percent carbon in the open type of furnace. It was because of the difficulty of getting that high carbon that they abandoned the roofed furnace and adopted the open furnace where the charge was melted in the smothered arc, and thus obtained three percent of carbon.

[1] Vice-President, The Electric Furnace Constr. Co., Media, Pa.
[2] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 10, 1920, President Bancroft in the Chair.

THE REDUCTION OF MANGANIFEROUS SILICATE SLAGS.[1]

By Edward F. Kern.[2]

ABSTRACT.

Experimental reduction of manganese-bearing slags in an electrice furnace, to produce manganese-silicon-iron alloys. Calculations show the percentages of manganese, silicon and iron reduced and escaping reduction, also the proportions volatilized. Calculations are made of the theoretical power needed for reduction and as sensible heat in the products, and the net thermal efficiency of the electric furnace operations is determined.

As an addendum, lead blast furnace slag was similarly treated, distilling off, however, 75 percent of the lead and 70 percent of the zinc present, and recovering 91 percent of the iron, 95 percent of the manganese, and 62 percent of the copper, as a metallic alloy. [J. W. R.]

The slags which are ordinarily produced in the melting of ferromanganese, preparatory to making of steels high in manganese by the Hadfield process, contain from 35 to 50 percent MnO, 45 to 40 percent SiO_2, and 5 to 10 percent $FeO + Al_2O_3$.

The high manganese content of these slags suggested the possibility of reducing them in an electric furnace with the idea of producing a desirable ferromanganese-silicon alloy, containing from 40 to 80 percent manganese, 30 to 40 percent silicon, and the balance iron.

The reduction of both silica and manganese oxide can be readily accomplished in the electric furnace: silica is reduced by carbon at 1460° C., and manganese oxide is reduced by carbon at 1105° C. A mixture of the two oxides may be reduced with the pro-

[1] Manuscript received February 13, 1920.

[2] Professor of Non-ferrous Metallurgy, Columbia University.

duction of manganese-silicon alloy, the composition of which will depend upon the proportion of the two oxides in the mixture. If an excess of carbon is present, carbides of both manganese and silicon are formed. The presence of metallic iron lowers the temperature necessary for the reduction of both manganese oxide and silica, and also of a mixture of the two oxides. With manganese silicate, the presence of iron in some form enables the production of ferromanganese-silicon in the electric furnace.[3]

Ferromanganese-silicon alloys are produced in the following ways: (a) The production of ferrosilicon in an arc furnace, and of ferromanganese in an arc-resistance furnace, and mixing the two molten alloys in such proportion as to make an alloy of the desired manganese, silicon, and iron content; (b) Reduction of a mixture of quartz and manganese oxides in an electric furnace by means of coke or anthracite, in the presence of iron oxide or metallic iron; (c) Reduction of manganese silicate in an electric furnace by means of coke or anthracite, in the presence of iron in some form. The production of the alloy by either (b) or (c) requires but one furnace, and there is less labor necessary than by method (a), but there is higher loss of manganese by volatilization.[4]

Manganese is volatilized at the temperature of the electric furnace, so in order to reduce the volatilization losses the temperature of the furnace should be kept as low as practicable. On account of the extremely high local temperatures in an arc furnace, the arc-resistance type of furnace is better suited for the production of manganese-silicon alloys. The effect of metallic iron in the charge for the production of these alloys is shown by the following results: silica is reduced by carbon at 1,460° C.; when iron is present the reduction occurs at 1,200° C.; manganese oxide is reduced by carbon at 1,105° C.; in the presence of iron the reduction occurs at 1,030° C.[5]

The effect of silicon in ferromanganese alloys is the same as has been observed in high silicon pig iron, that is, it precipitates the carbon as graphite from the combined state; it can do this, however, only when the temperature at which is is produced is not so high and the amount of carbon is not so great that the silicon

[3] Stansfield: "The Electric Furnace" (1914), 265, 266, 267, 278.
[4] U. S. Bureau of Mines Bulletin No. 77 (1914), 102-185.
[5] U. S. Bureau of Mines Bulletin No. 77 (1914), 145.

itself tends to form a carbide. The metal manganese resembles iron in many particulars, but is more difficult to reduce from its ores. Silicon-eisen, or "glazed pig," which is low-grade ferrosilicon containing some 10 to 15 percent of silicon, can be made in the blast furnace by using silicous charges and a great excess of fuel, the silicon being derived from the silica in the charge. In the electric furnace, however, using quartz as the source of silicon, with coke to reduce the quartz to metallic state and some iron ore or scrap iron to alloy with the silicon, an alloy containing as much as 80 percent of silicon may be obtained. The electric furnace ferrosilicon has largely displaced the blast furnace product, as the cost of the former per unit of silicon is much less. Some other ferro-alloys are also made more cheaply in the electric furnace than in the blast furnace.[6] Carbonless silicon alloys can be produced in a furnace of the Héroult electric smelting and electric steel furnace types, in which the carbon electrodes do not touch the molten metal, but which make contact with the layer of molten slag which covers the molten metal.

B. G. Klugh presented a paper on the production of silicon-manganese in electric furnaces at the thirty-fifth meeting of the Society (New York City, April, 1919).[7] About 50 tons of alloy was produced, which had an average analysis of 65 percent Mn, 21 percent Si, 13 percent Fe, and below 1 percent C. The analyses of the raw materials charged to the furnace were as follows:

	Mn	Fe	SiO_2	Al_2O_3	CaO	MgO	BaO	H_2O
Ore	33.11	2.41	15.19	3.96	1.96	0.62	0.50	10.72
Ore	34.00	3.19	32.85	3.12	....	0.26	0.62	1.00
Ore	17.87	2.96	32.97	8.72	0.39	0.50	1.10	22.20
Limestone	....	....	0.90	0.42	54.87	0.75	....	....

The ores and limestone were mixed so as to produce a free flowing slag running 36.34 percent SiO_2, 37.04 percent CaO, 1.71 percent MgO, 15.28 percent Al_2O_3, 2.39 percent BaO, and 5.21 percent Mn.

The reducing agent used was Alabama bituminous coal containing 54.0 percent fixed carbon, 21.0 percent volatile matter,

[6] Stansfield: "The Electric Furnace" (1914), 267.
[7] Trans. Am. Electrochem. Soc. (1919), 35, 401.

0.85 percent Fe, 10.0 percent SiO_2, and 8.15 percent Al_2O_3.

Seventeen hundred and fifteen pounds of reducing carbon and 168 pounds of electrode were used per ton (1,895 kg. and 185 kg. per metric ton) of metal reduced. The ratio of ore smelted to metal reduced was 3.53 to 1; 73 percent of the manganese in the charges was found in the metallic alloy, 10.02 percent went into the slag, and 16.98 percent (by difference) was volatilized. Forty-three hundred and fifty-eight pounds of slag was produced per 2,000 pounds (2,174 kg. per metric ton) of alloy reduced. The power consumed was 9,000 kw. hours per 2,000 pounds (9,900 kw. hour per metric ton) of alloy reduced.

B. G. Klugh also reported the reduction of manganiferous slags in an electric furnace for the production of ferromanganese-silicon alloys. A fair average analysis of the manganiferous slag treated was 20.0 percent Mn, 34.0 percent SiO_2, 14.0 percent Al_2O_3, 25.0 percent CaO, 2.0 percent MgO, and 1.5 percent BaO. About 100 tons of alloy was produced, containing about 70 percent Mn, 20 percent Si, 9 percent Fe, and below 1 percent C. The residual slag was of a rather sluggish and sticky nature, tending to form accretions in the furnace; its analyses averaged 29.12 percent SiO_2, 42.16 percent CaO, 2.73 percent MgO, 23 percent Al_2O_3, 1.61 percent BaO, and 1.0 percent Mn. About 96 percent of the manganese in the manganiferous slag treated was recovered in the reduced alloy, and 9,400 pounds of the residual slag was produced per ton (10,300 kg. per metric ton) of alloy recovered. The current consumption was 15,000 kw. hours per ton (16,500 per metric ton) of alloy; the high power consumption being due primarily to the large amount of residual slag.

EXPERIMENTAL PART.

The chemistry of the production of ferromanganese-silicon alloys by the reduction of manganiferous silicate slags is comparatively simple: the slag is a polysilicate, but regarding it as a mixture of combined or mutually soluble oxides, its reduction is then possible by merely mixing it with a suitable reducing agent and heating the mixture at a suitably high temperature to bring about the reduction. The composition of the manganiferous slag which was used for the experiments reported in this article was between 40 and 45 percent SiO_2, 45 to 50 MnO, and 10 to 5

$FeO + Al_2O_3$. A slag of this composition may be indicated by the formula $6MnO.FeO.7SiO_2$ (theoretical composition: 45.75 percent SiO_2, 46.40 percent MnO, and 7.85 percent FeO). The equation which indicates complete reduction of all of the manganese, silicon, and iron is:

$$6MnO.FeO.7SiO_2 + 21C = 6Mn.Fe.7Si + 21CO$$

The alloy produced according to this reaction would contain 56.70 percent Mn, 9.62 percent Fe, and 33.68 percent Si, which is higher in silicon and lower in iron than is usually desired. The control of the composition of the resulting alloy can be readily accomplished; the percentage of iron can be increased by the addition of either metallic iron or iron oxide; and the percentage of silicon decreased by the addition of twice the weight of lime as silicon to enter the slag, the lime to combine with an equivalent of silica to form calcium by-silicate ($CaSiO_3$), which is reduced at temperatures far above the reduction temperature of manganese silicate. This is illustrated by the following equation:

$$6MnO.FeO.7SiO_2 + 2Fe + CaO + 19C = 6Mn.3Fe.6Si + CaSiO_3 + 19CO$$

The alloy produced according to this equation would contain 50 percent Mn, 25 percent Fe and 25 percent Si, which indicates that by mixing the manganese silicate slag with calculated amounts of lime, carbon, and either metallic iron or iron oxide, alloys of any desired composition may be produced. The reduction of large quantities will have to be done in an electric furnace of such a type that no excess of carbon is taken up by the resulting alloy, preferably in a furnace of the arc-resistance type (Héroult, Girod, Keller, etc.). The composition of the resulting alloy may be controlled by the proper proportioning of the materials composing the charge. The temperature of the reduction must be such that the loss of manganese by volatilization is held at the minimum, and below that at which normal carbides are formed.

The experiments were conducted in the electro-metallurgical laboratory of the School of Mines of Columbia University. Runs Nos. 13 to 18. inclusive, were made by Mr. A. J. Mandell, a

student in the School of Mines. The results of these runs confirmed those of Runs Nos. 1 to 12, inclusive, which were made by the author.

In order that the different portions of slag composing the charges of all of the runs (Nos. 1 to 18, inclusive) would be of the same composition, two 50-pound portions (45 kg.) of the commercial manganiferous slag were melted in a Dixon graphite crucible in a gas-fired crucible furnace, then thoroughly stirred and quickly poured upon a large cast-iron plate, which rapidly cooled the slag as thin sheets, and prevented segregation. The sheets of slag were crushed to pass through a 20-mesh screen, the fine material was thoroughly mixed, and a final sample taken for analysis. Two lots of slag were thus prepared: that which was used for Runs Nos. 1 to 12, inclusive, contained 43 percent SiO_2, 49 percent MnO, 5 percent FeO, and 4 percent Al_2O_3, equivalent to 20.2 percent Si, 38 percent Mn, 4 percent Fe, and 37.7 percent oxygen (by difference); the slag which was used for Runs Nos. 13 to 18, inclusive, contained 42 percent SiO_2, 46 percent MnO, and 12 percent FeO, equivalent to 19.7 percent Si, 35.6 percent Mn, 9.3 percent Fe, and 35.4 percent oxygen (by difference).

The charges for all of the runs were calculated so as to produce an alloy of a certain composition, for instance: 50 percent Mn, 25 percent Fe, and 25 percent Si; 60 percent Mn, 20 percent Fe, and 20 percent Si; 40 percent Mn, 36 percent Fe, and 24 percent Si; 46 percent Mn, 27 percent Fe, and 27 percent Si. In calculating these different charges, endeavor was made to vary the percentage of silicon in the resulting alloy by varying the amounts of lime added to form $CaSiO_3$, so that some check on the effect of the lime could be obtained; the percentage of iron in the alloy was varied by the addition of varying amounts of metallic iron in small pieces. The amount of carbon for the reduction was calculated in accordance with the equations previously given, the amount of carbon required being 75 percent of the weight of oxygen to be removed, as carbon monoxide. The more lime which was added to the charges, the less carbon was required, because there was less SiO_2 to be reduced. The anthracite which was used as the reducing agent contained 90 percent carbon.

The charges were thoroughly mixed, placed in an Acheson graphite crucible, and the reduction was made in a 20 kw. Hoskins carbon-plate resistance furnace. The use of Acheson graphite crucibles introduced carbon in excess, but as no other refractory crucibles which were available could withstand the temperature at which the reduction occurred, the Acheson crucibles had to be used. The current required to heat the furnace was approximately 1,100 amperes with from 19 to 20 volts drop between terminals. When the tests were completed, the crucibles were removed from the furnace, and the contents poured into an iron mold and allowed to solidify. When the alloy was cool, the button and the residual slag were separated, and both weighed. Several of the buttons (of Runs Nos. 3, 4, 5, 6 and 7) were analyzed, but lack of time prevented the analysis of all of them. From the weight of the manganiferous slag composing the charge, and the weight of the resulting alloy, the percentage recovery and the percentage reduction were calculated. The temperature of the crucible in the furnace was determined by means of a Wanner optical pyrometer which was sighted upon the side of the crucible through a small hole in the cover of the furnace. It was noticed that the temperature at which reduction commenced was indicated by the formation of dense, heavy, brown to yellow fumes of manganese oxide. This occurred when 1,470° C. was reached, below which scarcely any metal was formed, and approximately 500° C. above the melting point of the slag which was being reduced. A representative sample of the slag was heated above its melting point, and then allowed to cool slowly. It started to melt at 1,010° C. and was completely molten at 1,055° C.; during cooling it started freezing at 1,040° C. and was completely solid at 975° C.

The results of the experiments are given in Table I.

Four preliminary runs were made in order to determine at what temperature reduction of the manganiferous slag started; these four charges were similar to those of Runs 1, 2, 3, and 4. The temperature was brought up to 1,450° C., and held for 45 minutes. In no case was any fume of manganese oxide noticed coming from the crucibles, also no metal was found in any of the crucibles. These preliminary runs confirmed previous experiments, in that reduction of manganese silicate slags does not take

TABLE I.

Run No.	Grams of Slag Treated	Slag contains grams of			Grams added to Charge.			Grams of Carbon.		Silicon as SiO_2 slagged by the lime added.	Temperature when reduction started, °C.	Maximum temperature reached, °C.	Time of heating above 1450° C. Minutes.	Total Weight of Alloy.	Grams of available metals in slag.	Grams of available metals recovered from slag.	Percentage of available metals recovered from slag.
		Manganese.	Silicon.	Iron.	Metallic Iron.	Lime.	Anthracite.	Required.	Added.*								
1	400	152	81	16	0	0	117	113	105	0	1475	1600	120	112	249	112	45
2	400	152	81	16	0	20	140	105	126	10	1475	1600	120	110	239	110	46
3	800	304	162	32	0	0	250	226	225	0	1470	1525	75	95	498	95	19
4	800	304	162	32	150	0	250	226	225	0	1475	1550	75	285	498	135	27
5	500	190	101	20	100	0	100	141	90	0	1475	1580	135	268	311	168	54
6	500	190	101	20	100	148	50	79	45	74	1470	1575	120	239	237	139	59
7	500	190	101	20	0	148	50	79	45	74	1475	1625	120	165	237	165	70
8	450	171	91	18	0	0	150	128	135	0	1470	1620	135	160	280	160	57
9	450	171	91	18	0	0	90	128	81	0	1470	1560	150	216	280	216	77
10	450	171	91	18	90	0	90	128	81	0	1470	1545	150	294	280	204	73
11	450	171	91	18	0	114	50	80	45	57	1475	1540	150	194	223	194	90
12	450	171	91	18	90	114	50	80	45	57	1475	1525	150	225	223	135	67
13	500	178	98	46	100	0	150	133	135	0	1470	1600	150	205	323	105	33
14	500	178	98	46	50	0	150	133	135	0	1470	1610	120	175	323	125	39
15	700	249	138	65	70	0	210	186	189	0	1470	1560	120	260	452	190	42
16	500	178	98	46	80	60	110	107	99	30	1475	1610	75	215	292	135	46
17	500	178	98	46	50	50	100	112	90	25	1470	1600	135	170	297	120	41
18	500	178	98	46	30	0	0	133	0	0	1470	1590	150	240	322	210	65

* The deficiency of carbon was supplied by the graphite crucible.

place at temperatures below 1,450° C. The temperature at which reduction starts and at which it ceases was found to be indicated by the giving off of dense brown to yellow fume, when reduction ceased no more fume was seen coming from the crucibles, which was about 1,550° C. It was found that normal carbides formed if the temperature was carried above 1,600° C., and the longer and the higher the temperature was kept between 1,600° and 1,700° C., the more carbides were produced. The temperature at which the most efficient reduction of the manganiferous slags occurred was between 1,525° and 1,575° C.; neither the presence of metallic iron in the charge nor the slagging of part of the silica by the addition of lime to the charge seemed to affect the reduction-efficiency. The presence of metallic iron in the charge, however, seemed to bring about a higher recovery of silicon; and the addition of lime controlled the amount of silicon entering the resulting alloy. All of the alloys produced were lustrous and brittle.

The analyses of five of the resulting alloys show the effect of the additions of metallic iron and of lime to the charges. These five alloys were typical of the other alloys produced by the other runs.

TABLE II.

Analyses of Alloys from Runs Nos. 3, 4, 5, 6, and 7.

From Run No.	Silicon Percent	Manganese Percent	Iron Percent	Aluminum Percent	Carbon Percent
3	16.9	77.6	3.7	0.2	1.33
4	11.6	38.0	47.0	0.5	2.73
5	19.4	48.5	29.7	0.2	1.88
6	5.7	38.8	50.1	0.2	4.70
7	9.7	83.7	3.5	0.3	....

The analyses of these alloys also show what effect the silicon content of the alloy has upon the amount of carbon retained by the resulting alloy—the higher the silicon, the lower the carbon.

The theoretical power required to produce ferromanganese-silicon alloys in a commercial electric furnace by the reduction of the manganiferous silicate slags was calculated similarly to the calculations given on pages 162 and 163 in Bulletin 77 of the

Bureau of Mines. The values which were used in making the calculations are the following:

The heat supplied for the reduction of:

1 Kilogram of Fe from Fe_2O_3	1746 Kg.	Cals.
1 " " Fe " FeO	1175 "	"
1 " " Mn " MnO	1653 "	"
1 " " Si " SiO_2	7000 "	"
Heat of oxidation of 1 kilogram C to CO	2430 "	"
Heat liberated by 1 kilogram CaO forming $CaSiO_3$	319 "	"

The average Specific Heat, between 1200 and 1600°C. of: Iron = 0.20; Manganese = 0.35; Silicon = 0.37; Carbon = 0.55; Lime = 0.38; Slags = 0.33; Carbon monoxide = 0.30.

1 Kilowatt-hour equivalent to 857 Kilogram-calories.
1000 Kilograms equals 2200 pounds.

In making the calculations it was assumed that the loss of manganese by volatilization was 20 percent, the manganiferous slag which was not reduced as being 20 percent, and the heat efficiency of the electric current supplied to the furnace as being 55 percent. The figures which were obtained are as follows.

The calculations were made on Runs Nos. 5, 6, 7, and for a theoretical charge and reduction which would produce an alloy containing 50 percent Mn, 25 percent Si, and 25 percent Fe. The theoretical power consumed in producing 2,000 pounds of alloy corresponding to that of Run No. 5 will be approximately 4,400 kilowatt-hours (4,840 per metric ton); for producing 2,000 pounds of alloy corresponding to that of Run No. 6 approximately 3,100 kilowatt-hours (3,410 per metric ton); for producing 2,000 pounds of alloy corresponding to that of Run No. 7 approximately 5,100 kilowatt-hours (5,610 per metric ton); and for producing an alloy corresponding to the theoretical alloy (50 percent Mn, 25 percent Si, and 25 percent Fe) it would require 4,600 kilowatt-hours per 2,000 pounds (5,060 per metric ton). These figures show that the power consumption is greatest for the alloys running highest in manganese and lowest in iron, and *vice versa*. It is also evident that the lower the manganese in the manganiferous slag the greater will be the power consumed in producing a ferromanganese-silicon alloy of a definite composition, because a larger amount of residual slag will be made. This is shown to be the case by the work done by Klugh, who found that it required 15,000 kilowatt-hours per 2,000 pounds of alloy (6,500 per metric ton) containing about 70 percent Mn,

20 percent Si, and 9 percent Fe recovered by the reduction of manganiferous slag containing 20 percent Mn, 34 percent SiO_2, 14 percent Al_2O_3, 25 percent CaO, and the residual slag running 29.12 percent SiO_2, 42.16 percent CaO, 2.73 percent MgO, 23.0 percent Al_2O_3, and 1.0 percent Mn; about 9,400 pounds of residual slag produced per 2,000 pounds (10,300 kg. per metric ton) of the alloy recovered.

ADDENDUM.

Electric Reduction of Lead Blast-Furnace Slag.

A trial run on the reduction of lead blast-furnace slag was made in the same manner as for the reduction of the manganiferous slag. The original slag contained 31.2 percent SiO_2, 27.6 percent Fe (35.6 percent FeO), 2.1 percent Mn (2.7 percent MnO), 14.0 percent CaO, 7.9 percent Al_2O_3, 0.95 percent Pb, 4.0 percent Zn, 0.16 percent Cu, 0.59 ounces Ag, and 0.0025 ounces of Au per 2,000 pounds (907 kg.).

Five hundred grams of the pulverized lead slag was mixed with sufficient pulverized coke (50 grams) to reduce the oxides of iron, manganese, lead, zinc, and copper, and sufficient lime (182 grams) to combine with the silica and form a residual slag low in iron and manganese and high in lime. The charge was well mixed and passed through a ¼-inch (0.6 cm.) screen, then placed in an Acheson graphite crucible, and heated in the Hoskins carbon resistor furnace. The temperature was brought up to 1,520° C. At 1,170° C. zinc began to distill and ceased to be given off when 1,430° C. was reached; ten minutes later the temperature had reached 1,520° C., when the operation was stopped and the contents of the crucible emptied into an iron mold.

Five hundred grams of the original lead slag contained 156 grams of SiO_2, 70 grams of CaO, 39.5 grams of Al_2O_3, 138 grams of iron, 10.5 grams of manganese, 20 grams of zinc, 4.75 grams of lead, and 0.8 gram of copper. The resulting metal weighed 145 grams, or 29 percent weight of the original slag, and contained 87.02 percent iron, 7.0 percent manganese, 0.35 percent copper, a trace of zinc, and no lead. The amount of metal recovered as alloy was 126 grams of iron (91.3 percent recovery), 10 grams of manganese (95+ percent recovery), and 0.5 gram of copper (62 percent recovery).

The residual slag, which was similar in appearance to ordinary iron blast furnace slag, weighed 487 grams, or 97.4 percent of original slag; it contained 41.12 percent SiO_2, 46.78 percent CaO, 8.15 percent Al_2O_3, 2 percent Fe, 0.07 percent Mn, 0.2 percent Pb, 1.25 percent Zn, and trace copper. The metals remaining in the residual slag were 10 grams of iron, 0.34 gram of manganese, 1.0 gram of lead, and 6.1 grams of zinc. The amounts of lead and zinc distilled during the reduction were 3.75 grams lead (75 percent of original slag content), and 13.9 grams of zinc (70 percent of original slag content).

The theoretical power required to recover 2,000 pounds (907 kg.) of metal from 6,900 pounds (3,136 kg.) of the lead blast furnace slag by mixing it with 2,510 pounds (1,140 kg.) of lime and 690 pounds (434 kg.) of coke, and reducing it in an electric furnace, was calculated in same manner as was done for the ferromanganese-silicon alloys. The values which were used in calculating the heat supplied for the reduction of the oxides of lead, zinc, and copper are the following:

1 Kilogram of	Pb	from	PbO	.....	245	Kg.	Cals.
1 "	" Cu	"	CuO	.....	600	"	"
1 "	" Zn	"	ZnO	.....	1305	"	"

The average Specific Heat, between 1200 and 1600°C. of Lead = 0.09; Copper = 0.144; Lime = 0.367.
Heat in 1 kilogram of zinc vapor at 1300°C. = 588 Kg. Cals.

Assuming the efficiency of utilization of the heat energy of the electric current supplied as being 55 percent, the theoretical power consumed in producing 2,000 pounds of alloy corresponding to that obtained in this run will be 4,800 kilowatt-hours (5,280 per metric ton).

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A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 10, 1920, President Bancroft in the Chair.

STEP INDUCTION REGULATOR FOR ELECTRIC FURNACES.[1]

By PHILIP B. SHORT.[2]

ABSTRACT.

A description of the most recent development in electrical control equipment for electric furnaces. This consists of a combination induction-type regulator, a selector switch, a transfer switch, a series transformer, and a suitable panel for meters and switches. The illustrations and detailed description are of equipment recently designed for twenty electric zinc furnaces in Norway.—J. W. R.

The present type of arc furnace used for the melting and refining of steel is for the most part a furnace requiring not more than one or two operating voltages. In the smaller-sized arc furnaces one operating voltage is generally sufficient, whereas in the larger sizes two operating voltages are often desirable. The higher operating voltage is used for the melting of the cold charge and the lower voltage is employed during the refining stage. When an arc furnace is operating on a constant voltage the power input can be varied by moving the electrodes and thus lengthening or shortening the arc.

In contrast to the arc furnace there is the resistance furnace, and the furnace of the submerged arc type, where the electrodes are stationary. In these furnaces the load is largely a straight resistance load, the charge itself often making up the resistor. In this case a varying voltage is desirable, for the resistance of the load will change as the temperature rises, and means are required for controlling the input of power into the furnace. Re-

[1] Manuscript received December 11, 1919.

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sistance furnaces and furnaces requiring a variable voltage supply are rapidly increasing in number, and are now in use for graphite, brass, zinc, carbon-bisulphide, heat-treating and numerous other uses.

FIG. 1. 1,100 K.V.A. Step Induction Furnace Regulator Equipment.

One of the most satisfactory means for supplying power to a furnace of the resistance type has been found to be the use of a combination step induction regulator. This consists, in the main, of a furnace transformer with taps in the primary winding, and an induction regulator for bridging between the voltages given by the transformer taps. With this combination, a continuous voltage, without breaks, can be secured over a wide voltage range.

A complete unit for this service consists of a furnace transformer, an induction regulator, a selector switch, a transfer switch, a series transformer, and a panel containing the necessary meters and control for the equipment. A 1,100 K.V.A. equipment of this type is shown in Fig. 1 and Fig. 4. These illustrations show one of twenty equipments that were recently manufactured for service on zinc furnaces, to be installed in Norway.

The transformer part of the unit has a low-voltage winding similar to that on any furnace transformer. The leads consist of heavy copper bars coming straight up from the winding, as is illustrated in Fig. 2. The leads are interlaced so that the reactance is kept to a minimum. Where a wide voltage range is desired, the low-voltage winding is made in two sections so that it may be placed in parallel for securing the lower part of the voltage range. The high-voltage winding is divided into three sections, as is shown in Fig. 3. One section forms the main winding, that is not changed throughout the voltage range. A second section (winding A) is not metallically connected to the primary circuit, and this is used for exciting the induction regulator. The third section is divided into many parts, and taps are brought out from each part, for connecting to the selector switch. By this means, various parts of the third winding may be cut out or in by the operation of the selector switch (S), as it is desired to raise or lower the furnace voltage. The taps coming from the high-voltage winding are shown in Fig. 2, coming to the terminal board within the transformer tank. From this point they are brought through bushings on the tank and connected to the selector switch.

The induction regulator is shown in Fig. 1 to the right of the transformer. It is immersed in oil and mounted in a corrugated iron tank. Above the regulator, on a pipe-frame mounting, are placed the selector and transfer switches. These are also immersed in oil. These switches are geared to the motor operating the induction regulator. The oil container in which the switches are mounted is counter-weighted, so that the inspection of the switch contacts can be very readily made. The control panel and instruments for the equipment are also shown in Fig. 1.

The operation of the step induction regulator can best be understood by referring to Fig. 3. The buck or boost of the induction

regulator is equal to one-half the voltage secured between adjacent transformer taps. From Fig. 3 it can be seen that the primary circuit is completed through the first section of the high-

FIG. 2. Inside View of 1,100 K.V.A. Furnace Transformer.

voltage winding, through the transfer switch *T*, through one coil of the series transformer *SR*, and through the selector switch to tap No. 1 of the transformer. The series transformer merely

insulates the induction regulator *R*, from the incoming high-line voltage, and the action is the same as though the secondary of the regulator were connected directly in the line. Any voltage induced in the secondary of the regulator is carried directly through to the line, by the series transformer. The induction

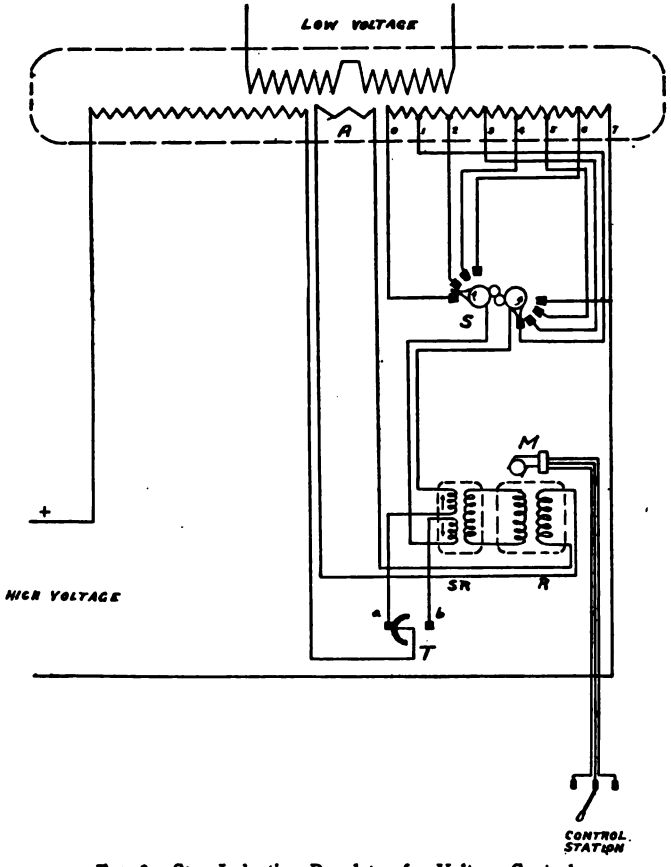

FIG. 3. Step Induction Regulator for Voltage Control.

regulator, therefore, adds to or subtracts from the normal line voltage in the same manner as though the series transformer were not used. When the induction regulator is in the neutral position, no voltage is added to or subtracted from the incoming supply voltage.

When it is desired to vary the furnace voltage, it is merely necessary to start the operating motor *M*, of the regulator, and immediately a voltage is induced in the secondary of the regulator. In order to raise the furnace voltage, this induced voltage would be such as to add to the supply voltage. With the regulator continuing to revolve, the induced voltage would reach its maximum

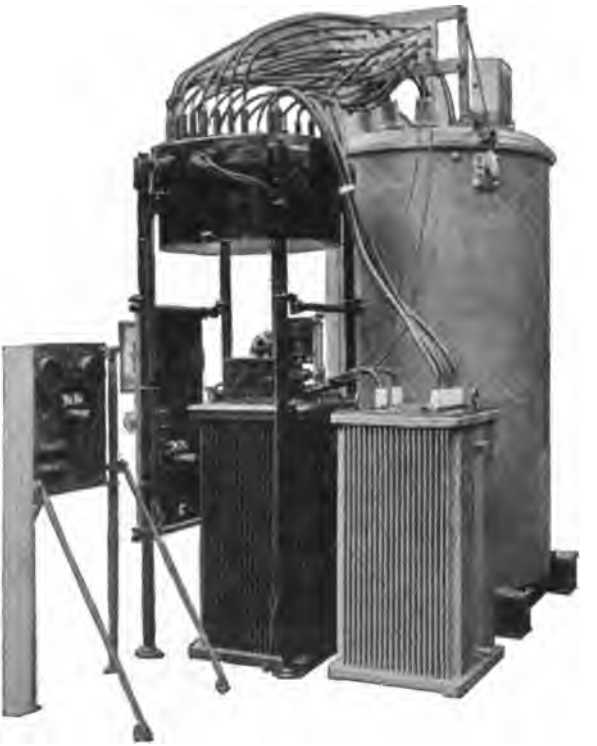

FIG. 4. 1,100 K.V.A. Step Induction Furnace Regulator Equipment.

value, which is one-half the value obtained between adjacent transformer taps. At this point, the selector switch *S*, being geared to the regulator, acts so as to connect the next transformer tap (No. 2), to the supply. At this same point, the transfer switch *T*, which is also geared to the regulator, acts so that the induced voltage in the regulator subtracts from, rather than adds to, the supply voltage. This last operation is secured by having

the secondary of the series transformer made up of two windings, so that the reversal from boost to buck can be made through the transfer switch by reversing one of these windings. This feature allows the induction regulator to be rotated continuously in one direction, for either raising or lowering the furnace voltage. As the regulator continues to rotate, it again arrives in its neutral position, and at this point the supply voltage is applied directly to tap No. 2. This same operation is repeated in transferring from tap to tap until the entire voltage range available is secured.

For lowering the furnace voltage it is merely necessary to reverse the direction of rotation of the regulator motor, and the operation is otherwise the same as described in going from tap to tap. From this, it can be seen that the function of the induction regulator is in bridging between the voltages secured from the various transformer taps. The selector switch serves as a means for connecting the various taps to the incoming supply line. The transfer switch permits the regulator to be rotated in one direction for either raising or lowering the voltage. The series transformer is used to insulate the induction regulator from the high-line voltage. Where the supply voltage is comparatively low, this transformer is not used. In this case the general operation is the same, except that the induction regulator has two secondary windings taking the place of the two windings provided on the secondary of the series transformer.

With this equipment, any voltage within the range can be secured at the furnace, by the simple operation of the control handle mounted on the switchboard panel. The apparatus may also be controlled entirely automatically by a constant current regulator. This can be arranged so as to maintain either constant current or constant energy within the furnace. The automatic control is shown mounted on the panel in Fig. 1.

The capacity of the induction regulator is small as compared to the capacity of the main transformer, for the regulator is used merely in bridging between adjacent transformer taps. Because of this, the efficiency and power factor of the equipment are not appreciably affected by the control. The entire equipment is designed to withstand the stresses of the severe load fluctuations which are encountered in furnace service, and no external reactance is required for the protection of the apparatus. Load cur-

rent is never broken by the selector or transfer switches, so that there is always energy input to the furnace, even while a change in voltage is being made. There is practically no arcing on the switch contacts, for the current that the switches are required to break is only the small circulating current that may flow during the transfer.

The equipment described represents the most recent development resulting from extensive experience in supplying electrical equipment for the electric furnace industries. The control of energy input to an electric furnace has become a matter for special consideration since the coming of furnaces in which are concentrated large amounts of power. The closest control of furnace voltage and energy input to the furnace is important from an economic standpoint, since the product becomes more uniform and the process more efficient when operating on the proper voltage. To the manufacturer, the former represents a higher price for his product, and the latter a lower manufacturing cost.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

CARBON IN IRON.[1]

By T. D. Yensen.[2]

ABSTRACT.

The ordinary method of determining carbon in iron and steel consists in burning the sample with pure oxygen, absorbing the CO_2 by means of KOH and weighing the KOH bulb before and after. In order to eliminate the errors due to absorption and weighing, the new method substitutes freezing out the CO_2 with liquid air and allowing it to expand into a known volume and noting the increase in pressure. In order to differentiate between the carbon existing as adsorbed CO or CO_2 and that existing in combined form, the method involves two heatings, one to 600° C. in vacuo, and the other to 1000° or higher in oxygen. Extra precautions are also taken to eliminate errors due to other sources, so that by this method carbon can, if necessary, be determined with an accuracy of ±0.0001 percent.

Introduction.

It has long been known that carbon has a great influence upon the properties of iron and iron alloys. On account of the small quantities of carbon involved—0.1 percent being regarded as a medium carbon steel—and the presence of carbonaceous matter in almost everything that is used in making chemical analyses, the correct determination of carbon in iron is the most difficult problem in iron and steel analysis. Not only are the total quantities of carbon very small, but carbon may exist in iron in various forms, one or more of which may influence the properties considerably, while others may have little or no influence upon these properties. The accurate determination of these small quantities

[1] Manuscript received Jan. 17, 1920.

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and the separation of the different forms is, therefore, of great importance, and a large amount of work has been done lately to discover suitable methods to accomplish this purpose.

In another paper, Mr. C. J. Rottman is giving an account of the various methods that have been and are being used for the determination of carbon in iron and steel. He is also describing certain improvements in the method of analysis in connection with the combustion method—particularly in regard to absorbing the CO_2—improvements that greatly diminish the errors in the analysis. However, even these improvements were not considered sufficient. The method described in this paper is a combustion method, but it eliminates some of the most important sources of error inherent in the standard method, namely those due to absorption and weighing, and makes it possible to decide accurately whether all the carbon has been burnt out of the sample.

The standard method consists in heating the sample—in the form of shavings or chips—in a gas-tight tube to a temperature of 800 to 1000° C., passing oxygen through the tube and absorbing the resulting CO_2 in a bulb containing KOH or the equivalent. The increase in weight of the KOH bulb gives the weight of CO_2. Precautions are taken, of course, so that presumably nothing but the CO_2 from the sample is absorbed by the KOH bulb. As ordinarily practiced this method is satisfactory for carbon content of 0.1 percent or more, and if great care is exercised the error should be within ± 0.01 percent. Mr. Rottmann states that with his improvements he is able to get an accuracy of ± 0.002 percent. While this may be correct when the analysis is done with painstaking care, it is very doubtful if better than $\pm$ 0.01 can be obtained with the analysis in the hands of a regular analytical chemist.

Errors in the Present Method.

The chief sources of error in the present method are:

1. Contamination of sample due to oil, grease, dust or dirt of any kind.

2. Dust or dirt or other carbonaceous matter in the combustion tube, in the sample holder, or in the connections between the tube and the rest of the apparatus.

3. Adsorbed CO or CO_2 in the walls of the combustion tube, or in the sample holder.

4. Admission of CO or CO_2 in opening the combustion tube.

5. Incomplete washing of the oxygen before it enters the combustion tube.

6. Incomplete oxydation of the carbon, resulting in some CO instead of all CO_2.

7. Incomplete absorption of CO_2 in the KOH bulb.

8. Weighing of the KOH bulb; moisture and dust collects on the bulb in uncertain amounts, and the weighing itself can at best be done with an accuracy of ± 0.1 mg.

9. Carbon left in sample.

Some of these sources of error can be eliminated in the present method by careful manipulation, thus

(1) can largely be taken care of by careful sampling and boiling the sample in ether prior to placing it in the combustion boat.

(2) and (3) can be minimized by burning out the system, including the sample holder, with oxygen, prior to introducing the sample, while

(5) can be easily eliminated by means of active KOH and soda-lime in the train, according to standard practice.

This leaves (4), (6), (7), (8) and (9) as sources of error that can not readily be eliminated when the present method is used. The resulting errors vary to such an extent that it is difficult to get satisfactory blanks, and it is, therefore, necessary to make radical modifications.

Mr. Ryder's Results.

Mr. H. M. Ryder has done a great deal of work on the elimination of gases from metals, including iron and iron-silicon alloys, by heating the samples in vacuo and analyzing the gases given off.[3] It was found that large quantities of CO and CO_2 were given off below 600° C., whereas additional CO was given off in varying amounts, depending upon the alloy, at and above the A_2 transformation point.

Based on these results it was concluded that the CO and CO_2 given off below 600° exist in the metal as adsorbed gases while the CO given off at and above A_2 is due to chemical reaction

[3] H. M. Ryder: "A Precision Method for the Determination of Gases in Metals." Trans. Am. Electrochem. Soc. (1918), 33, 197. "Analysis of Small Quantities of Gases." Jour. Am. Chem. Soc. (1918), 40, No. 11, 1656.

between the combined or graphitic carbon in the metal and the iron oxide present.

It is quite probable that these different forms of carbon, *i. e.*, that existing as adsorbed gases and that existing as combined or graphitic carbon, have different effects upon the physical properties of the metal and it is, therefore, of great importance to differentiate between them. This differentiation is taken care of in the new method as described below.

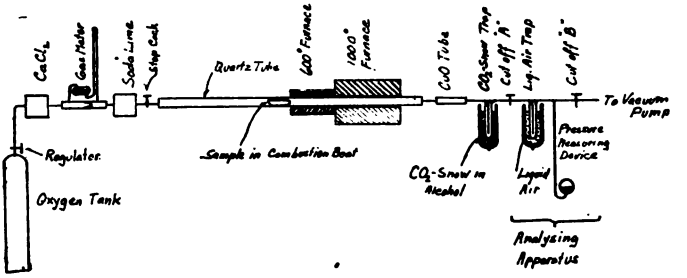

FIG. 1. Apparatus for Carbon Determination. (For details see Fig. 4.)

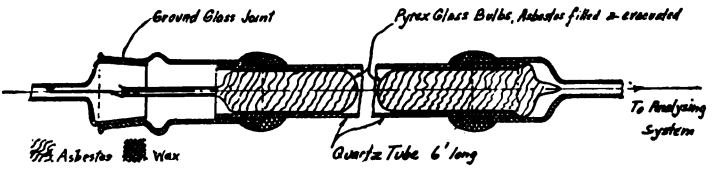

FIG. 2. Combustion Tube.

The New Method.

A sketch of the apparatus is shown in Fig. 1, and is self explanatory. The following is a condensed statement of the procedure:

(*a*) *Preparation of the Sample.*

The sample is carefully collected to keep out foreign matter and the weighed portion then cleaned with ether in the apparatus shown in Fig. 3. The ether is evaporated in an Erlenmeyer flask and the vapor passed through the sample held in the Gooch crucible. The condensed vapor again passes through the sample on its way from the condenser to the bottom of the flask and is reheated by the rising vapors. The sample is thus exposed to a

constant stream of hot, clean ether, carrying oily and greasy matter down into the bottom of the flask. This procedure should minimize source of error No. 1.

(b) Preparation of Combustion Boat and Tube.

The sample is then placed on a layer of specially prepared alundum in an alundum combustion boat that has previously been heated in the combustion tube to 1000° in a stream of oxygen. The sample is also covered with a layer of alundum. This precaution should eliminate carbonaceous matter in the boat and in the combustion tube (sources of error No. 2 and No. 3).

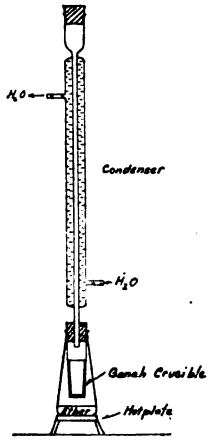

FIG. 3. Apparatus for Cleaning Sample.

(c) Elimination of CO and CO_2 Introduced into Tube while Open.

The combustion boat is now placed near the center of the tube with the furnaces moved over to one end, and the tube is closed. With the boat at room temperature or slightly above, the tube is evacuated to a pressure of 0.01 mm. Hg or better, eliminating all but traces of the free gases present in the system, thus eliminating source of error No. 4.

(d) Determination of Adsorbed CO and CO_2.

At the end of the above preliminary vacuum treatment, liquid air is placed on the trap and the 600° furnace is moved over the

sample. The sample is treated at 600° in vacuum for 15 minutes or more, in order to remove the adsorbed gases. The CO_2 is "frozen out" in the liquid air trap and the amount determined by isolating the analyzing apparatus, allowing the CO_2 to evaporate, and noting the increase in pressure.

(*e*) *Final Combustion.*

During the analysis of the CO_2 under (*d*), oxgyen is admitted to the combustion tube up to atmospheric pressure through the $CaCl_2$ and soda-lime bulbs to wash it free from H_2O and CO_2, the flow being regulated by means of the stop cock and regulator. This filling of the combustion tube requires about 10 minutes, and at the end of this period the previous analysis is completed and the combustion tube is evacuated through the CO_2–snow and liquid air traps. When the pressure reaches 0.01 mm. Hg cut off *A* is closed, the system further evacuated to 0.001 mm. and the CO_2 analyzed as before, at the same time filling the combustion tube a second time with oxygen to make another analysis to make sure that all the carbon has been removed.

Complete combustion of the carbon is ensured by passing the gases through CuO heated to 400°, eliminating source of error No. 6.

From the volume of the apparatus and the pressure, the amount of carbon can then be calculated. Absorption of CO_2 by KOH and weighing is thus done away with altogether, eliminating sources of error No. 7 and No. 8.

If there is any reason to believe that all the carbon has not been burnt during the previous combustion periods, the combustion process can be repeated any number of times until no further CO_2 is obtained. This can be done without introducing additional errors, which is not the case when the ordinary combustion method is used. Source of error No. 9 is thus eliminated.

Details of Apparatus.

(*a*) *Furnaces.*

The 1000° furnace is a platinum-wound furnace with a porcelain tube 24 in. (60 cm.) long and 1¾ in. (4.4 cm.) bore, insulated with fire clay and sil-o-cel. It can be maintained at 1000° with an input of 1 kw., and at 1400° with 3 kw.

The 600° furnace is 12 in. (30 cm.) long, 1¾ in. (4.4 cm.) bore, and consists of a silica tube wound with nichrome ribbon and insulated by means of magnesia pipe covering.

(*b*) *Quartz Tube.*

The quartz tube is 1⅜ in. (3.5 cm.) inside by 1⅝ in. (4.1 cm.) outside diameter by 6 ft. (180 cm.) long. One end is permanently sealed with a glass cap and cement, while the other end is provided with a ground glass joint.

(*c*) *The CuO Tube.*

The CuO tube is a Pyrex glass tube ⅝ in. (1.6 cm.) diameter, wound with asbestos and nichrome ribbon, without any heat insulation on the outside. It is filled with fine copper wire and heated to 400°.

(*d*) *Connections.*

All connections between the different parts of the apparatus are made with sealed hard glass tubing, eliminating sources of error due to leaks.

(*e*) *Analyzing Apparatus.*

The analyzing apparatus was constructed in accordance with a design originated by Mr. Ryder. A sketch of same is shown in Fig. 4. The apparatus is made from hard glass throughout. The sketch shows the mercury in the cutoffs in position ready for analyzing the CO_2 frozen out in the liquid air trap. The volume then includes the trap, the bulb of the McLeod gage and the connecting tubing. Up to the zero points of the mercury column the volume is 259 cc. As the pressure increases, the mercury falls in the various cut-offs, thus increasing the volume of the system. The volume, being a function of the pressure, was consequently determined for various pressures by means of the auxiliary bulb. Expressed in an equation the relation between the pressure and the carbon is:

$$C = (0.168 + 0.000095\ P)\ P,$$

where C = mg. of carbon and P = pressure in mm. Hg. Pressures up to 2 mm. are measured on the McLeod gage, while higher

pressures are measured by means of the difference in level of the mercury columns of the mercury pump cut-off. Pressures can be measured on the McLeod gage with an accuracy of ± 0.01 mm. Hg, and from the above equation it will be seen that this corresponds to a carbon content of ± 0.00168 mg. or ± 0.0000168 percent carbon if a 10 g. sample is used. This is far beyond the

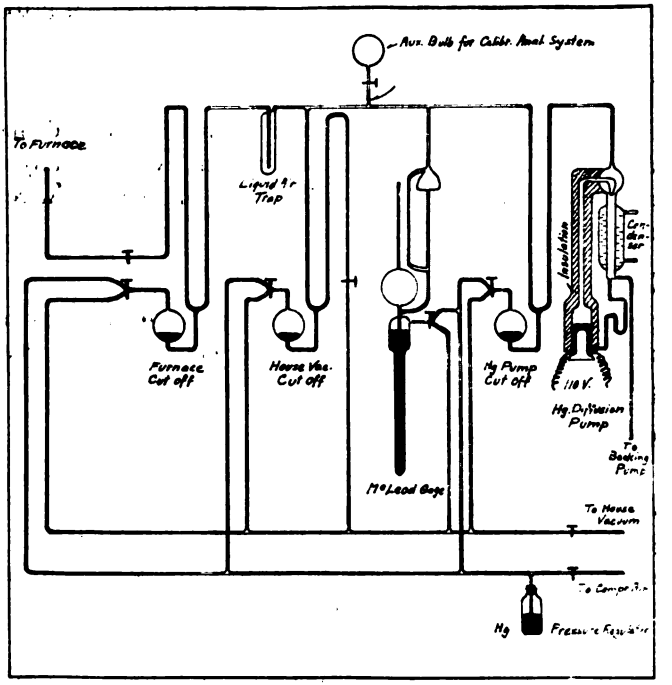

FIG. 4. Analyzing Apparatus for Carbon Determination.

required accuracy, so that no difficulty will be had in eliminating sources of error No. 7 and No. 8.

(*f*) *Diffusion Pump.*

The pump was constructed in accordance with the design developed by Mr. J. E. Shrader,[4] and is of the type that can be operated at fairly high backing pressures. It is capable of evacuating the system down to 0.0001 mm. Hg in 5 minutes.

[4] Westinghouse Research Laboratory. See Phys. Rev. N. S., Vol. 12, No. 1, July, 1918.

Preliminary Tests.

Numerous preliminary tests were made to weed out the weak points of the apparatus and to determine the limits of accuracy.

1. To determine the effectiveness of the various absorbing agents, a number of tests were made with ordinary air passing through properly prepared bulbs at a rate of 120 cc. per minute for 15 minutes, making a total of 1800 cc. The CO_2 escaping the first bulb was frozen out by liquid air in the analyzing system and the amount determined as usual. The result is shown in Table I.

TABLE I.

Efficiency of Various Absorbing Agents for CO_2.

No.	Absorbing Agent	Amount CO_2 in 1800 c.c. Air not Absorbed by Absorb. Agent mg.	Efficiency of Absorb. Agent Percent
1.	None	0.840	0
2.	KOH and $CaCl_2$.....	0.350	60
3.	Flemming Bulb (Soda lime).	0.025	97
4.	Liquid Air, Plain Trap.....	0.025	97
5.	Same, Trap filled with Glass Wool	0.001	99.9
6.	Same, Trap filled with Steel Wool	0.001	99.9

This shows that the rate used was too high for the KOH bulb but safe for the Flemming bulb. The plain liquid air trap passed 3 percent of the CO_2, while the traps filled with steel or glass wool passed only 0.1 percent of the total CO_2. Hence the adoption of the glass wool trap for the analyzing system.

2. A glass wool filled liquid air trap was at first also used in the purifying train, but it was found that the suction of this trap on the CO_2 given off in the furnace during the passage of the oxygen was sufficient to freeze out from 10 to 30 percent of the CO_2 given off. Furthermore, the liquid air trap in the purifying train necessitated passing oxygen through the furnace and the trap at a reduced pressure in order to keep the oxygen from liquifying in the trap. These considerations led to the adoption of the Flemming bulb for the purifying train. Table I shows that this bulb allows only 3 percent of the total CO_2 in the oxygen to pass through, and as the amount of CO_2 in the oxygen is very

small (only 0.02 mg. per 1800 c.c. as compared to 0.84 mg. for air) it is evident that the Flemming bulb is sufficiently effective.

3. Asbestos plugs were originally used at the exit end of the combustion tube to protect the wax seal from undue heating and no protection was used at all at the entrance end, where De Kotinsky cement was used to seal the glass to the quartz tube. It was soon found however that this arrangement caused a great deal of trouble, and the arrangement as finally adopted is shown in Fig. 2. The protecting bulbs at the ends consist of Pyrex glass filled with asbestos, evacuated and sealed off. They are securely held in place so that they cannot be drawn into the heated portion of the tube. They prevent heating of the wax very effectively without the use of materials in the combustion tube that absorb and give off gases in considerable and uncertain amounts.

4. Originally the house vacuum was used to evacuate the furnace down to a pressure of about 10 mm. Hg. The house vacuum was then cut off and the final evacuation done with a diffusion pump. However, large variations in the blanks (from 0.0005 mg. to 0.05 mg.) led to investigating the house vacuum system as a source of CO_2. The house vacuum—as the name implies—is used by the whole laboratory, and consequently there is a large variation in the pressure, ranging from a few mm. to 2 or 3 cm. Hg when someone is evacuating a large volume. It is conceivable that a sudden increase in the line pressure may cause a reverse current into the analyzing system and if there is any CO_2 in the line this will be frozen out in the liquid air trap. It was consequently decided to do all evacuation with the backing pump for the diffusion pump, and this resulted in a decided improvement. The apparatus in its final shape is therefore as shown in Figs. 1 and 2, using an individual pump for the evacuation.

With the furnaces cold and with no sample in the boat, but otherwise running the apparatus as usual, the amount of C obtained is only 0.002 mg. (with a variation of from 0.001 to 0.003 mg.).

With the furnaces heated as usual (to 600 and to 1000° C. respectively) and going through the regular procedure of analyzing a sample except that no sample is used, the following results are typical.

TABLE II.

Blanks of Apparatus.

Procedure same as usual, except no Sample in Boat.

Test No.	Tube Evac. Boat Cold		Boat heated in Vacuo to 600°			Boat heated to and at 1000° Tube filled with O_2, then evacuated.					
						1st Period			2d Period		
	Min.	Final Pressure mm.	Min.	Final Pressure mm.	Carbon Obt'd mg.	Min.	Final Pressure mm	Carbon Obt'd mg.	Min.	Final Pressure mm.	Carbon Obt'd mg.
104	23	0.010	11	0.000	0.013	27	0.010	0.029	..	....	....
108	14	0.015	20	0.003	0.027	26	0.010	0.025	25	0.010	0.030
124	51	0.002	20	0.001	0.017	36	0.005	0.038	40	0.005	0.044
Mean of 3 Tests					0.019			0.031			0.037
Variation from Mean					±0.007			±0.007			±0.007

The maximum variation in the blank is therefore less than ±0.010 mg. C, which for a 10 g. sample amounts to ±0.0001 per cent. For samples of different carbon contents the probable errors in the analysis are therefore as follows:

TABLE III.

Probable Errors in Samples of Various Carbon Contents.

10 g. Samples.

Carbon Contents		Errors in Analysis	
Percent	Mg.	Mg. (±)	Percent (±)
0.1000	10	0.01	0.1
0.0100	1	0.01	1.0
0.0010	0.1	0.01	10.0
0.0001	0.01	0.01	100.0

Results.

(a) *Electrolytic Iron.* A sample of doubly refined electrolytic iron serving as our standard of low carbon iron was analyzed according to the above method, giving the following results (shown graphically in Fig 5):

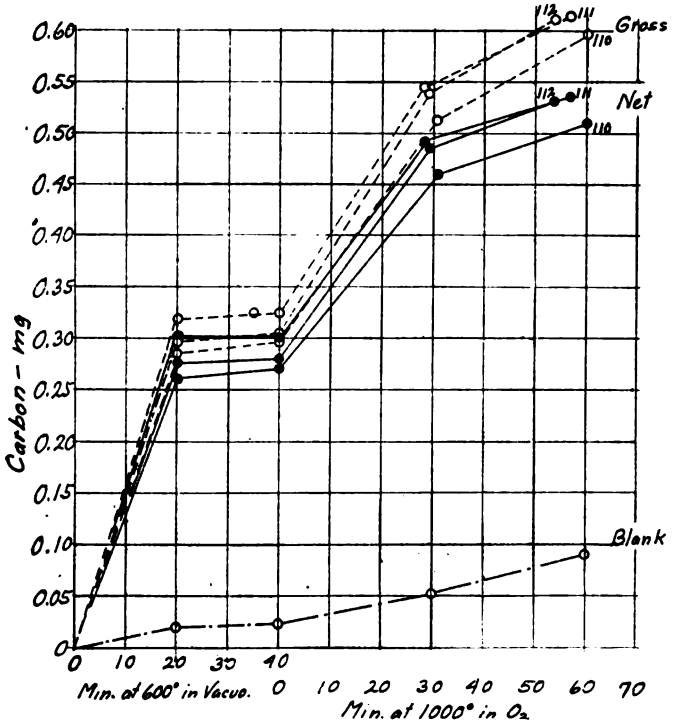

FIG. 5. Carbon in Electrolytic Iron. Standard Sample.

TABLE IV.

Carbon Content of Electrolytically Refined Iron. Standard Sample. 5 g. Samples.

Test Number	Sample Evac. Cold	Sample Heated in Vacuo to 600° *				Sample Heated to and at 1000°. Tube Filled with O_2 and Evac.								Net Carbon Obtained		
						1st Period				2d Period						
			Carbon Obtained				Carbon Obtained				Carbon Obtained			1st and 2d Car. Obt'd	Below 600° Adsorbed	At 1000° Combined	Total
	Min.	Min.	Gross Mg.	Blank Mg.	Net Mg.	Min.	Gross Mg.	Blank Mg.	Net Mg.	Min.	Gross Mg.	Blank Mg.	Net Mg.	Net Mg.	Percent	Percent	Percent
110	18	20	0.286	0.019	0.267	31	0.219	0.031	0.188	29	0.093	0.037	0.056	0.244	0.0053	0.0049	0.0102
111	15	20	0.320	0.019	0.301	28	0.220	0.031	0.199	25	0.067	0.037	0.030	0.229	0.0060	0.0046	0.0106
112	15	20	0.295	0.019	0.276	28	0.235	0.031	0.204	29	0.076	0.037	0.039	0.243	0.0055	0.0049	0.0104
														Mean of Three Samples	0.0056	0.0048	0.0104
														Variation from Mean (±)	0.0004	0.0002	0.0002

* Carbon eliminated during 2d Period at 600° in Vacuo is < 0.01 mg.

These results show that the total carbon content of this material is 0.0104 (±0.0002) percent. The important fact to be noted from these results is that of the total carbon content, more than half (0.0056 (±0.0004) percent) is in the form of adsorbed gases, such as CO or CO_2, given off at or below 600°, and that the combined carbon content is only 0.0048 (±0.0002) percent.

The above standard sample of electrolytic iron was carefully analyzed by Mr. C. J. Rottmann, according to the "Old" method, the average of 11 separate analyses being 0.0177 percent with a maximum variation from the mean of ±0.0080 percent. This amount includes all carbonaceous matter introduced into the combustion tube, *i. e.*, CO_2 admitted in opening and closing the tube, adsorbed gases and combined carbon.

In order to determine the amount of CO_2 admitted to the combustion tube while removing the old sample and introducing the new one, the gas was analyzed during the preliminary evacuation with the sample cold. Six tests gave values of carbon introduced in this way varying from 0.15 mg. to 0.67 mg. Based on a 5 g. sample this corresponds to 0.0030—0.0134 percent. The results are tabulated in Table V for the sake of comparing the "Old" and the "New" methods.

TABLE V.

Comparison of "Old" and "New" Methods of Analysis. Electrolytically Refined Iron. Standard Sample.

	"New" Method Mean of 3 Tests Percent C	"Old" Method Mean of 11 Tests Percent C
1. Carbon introduced while opening and closing combustion tube.....	0.0080 ± 0.0050	
2. Carbon as adsorbed Gases.....	0.0056 ± 0.0004	
3. Carbon in Combined Form.....	0.0048 ± 0.0002	
Total,	0.0184 ± 0.0050	0.0177 ± 0.0080

The results are in remarkably close agreement, both as to total carbon and as to variation. It will be noted that the variation is largely due to item 1, namely carbonaceous gases introduced into the combustion tube while opening and closing the tube, gases that have no connection with the sample at all, but amounting to

30–130 percent of the total carbon content (items 2 and 3). This fact explains the large variation usually obtained in the carbon content of low-carbon iron.

(b) *Vacuum Fused Electrolytic Iron.* Table VI shows some results obtained with electrolytic iron after being melted in a vacuum furnace and forged into rods. 2–202 and 2–210 were melted in an Arsem type furnace and 2–251 in a Tungsten wound furnace.

TABLE VI.

Vacuum Fused Electrolytic Iron. 5 g. Samples.

Test No.	Sample No.	Description of Sample	Net Carbon Obtained		
			600° Percent	1000° Percent	Total Percent
121	2-202	As forged. Outer half of Rod, except surface. Ether cleaned.....	0.0104	0.0159	0.0263
119	2-202	Forged and Annealed in Vacuo. All of Rod except surface. Not cleaned.....	0.0000	0.0038	0.0038
120	2-202	Forged and Annealed in Vacuo. All of Rod except surface. Ether cleaned...	0.0000	0.0045	0.0045
115	2-210	As forged. Outer half of Rod, except surface. Not cleaned.....	0.0027	0.0042	0.0069
116	2-210	As forged. Outer half of Rod, except surface. Ether cleaned	0.0015	0.0039	0.0054
113	2-210	As forged. Center of Rod. Not cleaned	0.0008	0.0031	0.0039
114	2-210	As forged. Center of Rod. Ether cleaned	0.0004	0.0030	0.0034
117	2-210	Forged and Annealed in Vacuo. All of Rod except surface. Not cleaned....	0.0009	0.0015	0.0024
122	2-251	As forged. Center of Rod. Ether cleaned	0.0006	0.0025	0.0031

Previous analyses by the "Old" method have given 0.02-0.04 percent Carbon for the above samples, *i. e.*, up to 10 times what the "New" method gives.

(c) *Bureau of Standards Samples.* As a check of the constants of the apparatus two of the Bureau of Standards standard steel samples were analyzed, the results being given in Table VII.

Judging from these results the agreement is as close as can be expected, and the conclusion is justified that the constants of the apparatus are correct.[5]

[5] It should be noted that for such large carbon contents, the accuracy of the apparatus is not as great as for smaller carbon contents, because in the former case the pressures are too large to be read on the McLeod gage and must be read on the barometer directly. In the above cases the pressures were in the neighborhood of 20 mm., and the readings can be read with an accuracy of only $\pm$ 0.5 mm., resulting in probable errors of $\pm$ 2.5 percent.

Modifications of the Method.

The apparatus as described in this paper is necessarily elaborate, especially the analyzing part of it, in order to eliminate all possible errors. However, great simplifications can be made to meet the requirement of different users. In another apparatus used in this laboratory the analyzing system consists of two good stopcocks, a liquid air trap, and a long mercury column similar to the arrangement shown in Fig. 1, and it gives very satisfactory results. Furthermore, split furnaces can be used, arranged on swinging arms, thus doing away with the long combustion tube. This modification would probably result in lower blanks, because the

TABLE VII.

Analysis of Bureau of Standards Standard Samples.
2 g. Samples.

No. 20a Acid Open Hearth Steel, 0.4 percent Carbon. Containing, according to the Bureau of Standards, 0.393 percent Carbon.
No. 15a Basic Open Hearth Steel, 0.1 percent Carbon. Containing, according to the Bureau of Standards, 0.109 percent Carbon.

Test No.	Sample	Net Carbon Obtained		
		600° Percent	1000° Percent	Total Percent
102	No. 20a	0.015	0.367	0.381
103	No. 20a	0.010	0.365	0.375
	Mean	0.0125	0.366	0.378
	Variation from Mean (±)	0.0025	0.001	0.003
105	No. 15a	0.005	0.112	0.117
106	No. 15a	0.009	0.094	0.103
107	No. 15a	0.006	0.101	0.107
	Mean	0.007	0.102	0.109
	Variation from Mean (±)	0.002	0.010	0.007

carbon obtained in the blanks is probably, in part at least, due to diffusion of CO_2 from the atmosphere through the heated portions of the tube. Finally the mercury diffusion pump may be eliminated, depending entirely on the oil pump for evacuation. This is done in the apparatus referred to above. In short, the apparatus can be made as simple or as elaborate as the requirements call for.

Summary and Conclusions.

1. It has been shown in this paper that by the method described great accuracy in determining the products of the combustion tube is possible; 0.001 mg. carbon can readily be measured by the analyzing system.

2. The blanks of the apparatus are small and consistent, the maximum variations amounting to only ± 0.007 mg. carbon, which is the probable error of the apparatus. This, for a 10 g. sample containing 0.01 percent carbon would result in an error of ± 0.00007 percent carbon or 0.7 percent of the total. This is 100 times better than is possible by any of the present methods.

3. By carrying out the analysis in three stages, namely (*a*) with the sample evacuated cold, (*b*) heated to 600° in vacuo, and (*c*) heated to 1000° in oxygen, it is shown that the total amount of carbon obtained from electrolytic iron is divided about equally between (*a*), (*b*) and (*c*); in other words, that about 0.005 percent is due to gases admitted to the tube in introducing the sample, that about 0.005 percent is present in the iron as adsorbed or occluded gas, and that the remainder 0.005 percent is the combined carbon.

4. A great deal of variation exists in the amount of carbon obtained during the first stage of analysis, (3*a*), and it has been shown that the great variations in the carbon contents of low carbon iron usually obtained may be attributed to this source.

5. The new method can be modified to suit any given condition; but for carbon contents of 0.10 and above the established methods, when carefully carried out, are sufficiently reliable to make more refined methods unnecessary. It is only for very low carbon contents that the errors in the established methods are so large as to conceal the true condition.

The author wishes to express his appreciation to Mr. A. L. Shields for his conscientious work in connection with the analyses and to Mr. C. J. Rottmann for his valuable advice based on his large experience in all matters pertaining to analytical chemistry.

Westinghouse Research Laboratory,
January 15, 1920.

DISCUSSION.

A. S. CUSHMAN[1]: The proposed method promises to shed some light on the much discussed question of the effect of gases in metallurgical products. A difference of hundredths of a percent of certain impurities is made the basis of acceptance or rejection under modern specifications. Under present methods of analysis carbon which may be present in steel as dissolved or occluded carbon monoxide is counted as combined or total carbon. It is not always understood that gases may be associated with steel in at least three separate states or conditions: (1) as the atmosphere in blow-holes or pipes, either large or invisibly small; (2) as gas molecularly entrained, sometimes spoken of as in solid solution; and (3) as combined with bases as oxides, nitrides, hydrides, etc.

Most of our present methods of analysis have decided limitations. The Ledebur oxygen determination measures only the oxygen in the form of reducible oxides. The method we have for nitrogen gets only that present as nitride and perhaps only part of that. The study of the effect of gases on the physical properties of metals is a most important as well as a much neglected field of investigation.

[1] The Inst. of Industrial Research, Washington, D. C.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

CARBON DETERMINATION IN FERRO-ALLOYS.[1]

By C. J. Rottmann.

Abstract.

Discussion of the difficulty of accurately determining carbon in ferro-alloys, and description of furnaces, absorbing apparatus and methods of operation by which accuracy to 0.002 percent can be consistently attained. Minute directions are given as to precautions in taking the sample, a new potash bulb for accurate and complete absorption is described, a nichrome-wound furnace for the combustion and its manner of use is described, and the accuracy attainable is discussed at length. [J. W. R.]

Difficulty has been experienced in determining the carbon content of ferro-alloys beyond the accuracy of the usual methods employed. Carbon in very small quantities, tenaciously held, greatly influences the magnetic properties.[2] For this reason it is important to know the carbon content in minute traces if possible. Carbon in magnetic alloys, as iron alloyed with silicon, cobalt, nickel, chromium, aluminum, etc., exists in several forms and may be conveniently classified into external, occluded, free and combined carbon. Carbonaceous material as grease or dust and adsorbed carbon dioxide may be included under external carbon, and is eliminated by proper preparation of the sample. Occluded and free carbon entrapped as CO, CO_2, hardening C or graphite together with the combined carbon are forms which influence the magnetic properties and to differentiate these from the external forms is desirable.

[1] Manuscript received Jan. 17, 1920.

[2] Westinghouse Research Laboratory, East Pittsburgh, Pa.

[3] Yensen: Trans. American Electrochem Soc., 37, April, 1920

Many methods of carbon determinations have been described in the literature and may be briefly summarized as follows:

Colormetric Method: For use on combined carbon; is approximately correct for materials containing over 0.1 percent carbon. Not accurate with certainty, and must be compared with standard sample similar to the one analyzed.

Metallurgical Examination: Method is approximate. It is of little use when sample contains less than 0.02 of C. The physical condition of the sample is important.

Oxidation of C to CO_2 by Wet Method: Fairly rapid for approximate work and accurate to a few hundredths percent of the carbon present, depending upon experience of analyst.

Combustion in Oxygen: Method most universally used; with care, results on carbon content may be accurate to a few thousandths percent of carbon, depending upon the method employed. The resulting CO_2 may be determined by adsorption and weighing, which is probably accurate to 0.004 percent, by precipitation and titration, accurate to 0.005 percent, by precipitation and resistivity, accurate to 0.006 percent, and by measurement of gas volume which can be estimated to 0.003 percent. By taking the average of many runs on combustion methods a result is obtained which is approximately correct, but only for that particular procedure. A sample of difficultly combustible ferro-silicon may give consistent results, but unless special precautions are taken to completely burn the last traces of carbide only relative results are obtained.

Where the carbon content of ferro-alloys is to be analyzed to ± 0.003 percent it is important that special care be exercised at all points in the procedure. Samples handled in the usual manner cannot check because of the varying composition due to external C. Electrolytic iron as sampled without treatment gave carbon contents as high as 0.07 percent, whereas the prepared sample gave results consistently at $0.014 \pm .001$ percent. The purifying train should be of sufficient capacity to handle efficiently 350 c.c. of gas per minute and quantitatively absorb all CO_2 present from the oxygen supply tank. A KOH tower, a $CaCl_2$ tube covered with soda lime, and a mercury manometer are desirable. The presence of moisture hastens the formation of CO_2 in the com-

bustion tube, hence the use of P_2O_5 is not necessary. Several types of furnaces were used, the electric furnace, described later, is preferable because of the freedom from external carbon. When using the granular carbon resistance furnace at high temperature the diffusion of carbon through the silica tube gives high results.

The selection of a thick-walled silica tube is important. Many thin-walled tubes soon become penetrable by carbon above 1200° C. The ends of the combustion tube should be well cooled so that no heating of the rubber stopper will occur. Copper tube ⅛ in. (3 mm.) diameter wound about the ends of the silica tube, through which cold H_2O may be circulated, serves very well for this purpose. See Fig. 1. Means should be provided to absorb any products of S, Cl, P, N, and H_2O occurring in the ferro sample

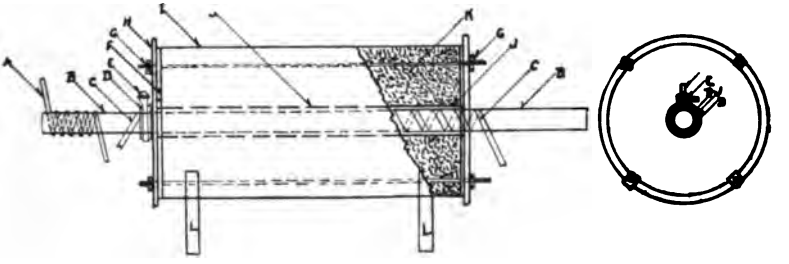

FIG. 1. Combustion Furnace.

before reaching the CO_2 analyzing apparatus. Where absorption bulb is used, care must be taken to get *complete* absorption. A special apparatus has been devised for this purpose and will be discussed later. Weighing errors are numerous and should be carefully corrected by the analyst. A comparatively long period of aspiration after burning each sample of difficultly combustible ferro-alloy is desirable, to be certain that all CO_2 is swept out of the apparatus. If oxidation is carried on too rapidly a fluxing action occurs which may entrap C. At the usual temperature of combustion slow diffusion of the trapped carbon takes place and it is eliminated by oxidation at or near the surface. Fluxing oxides, free from carbon, should be used with the more difficultly combustible alloys. This is especially true where silicon is used, because of the presence of silicon carbide. To exclude the effect of external carbon the sample was given the following treatment.

Preparation of Sample.

Uniformity as to size and shape of sample is important. See sampling in usual methods to obtain representative sample. Emphasis must be laid upon cleaning, when the carbon content is desired to ± 0.002 percent. The following treatment is recommended. Examine sample carefully to ascertain if any foreign substance is mechanically held, and that the drillings be oxide free. Extract the surface grease in porcelain thimble of Soxhlet apparatus. Transfer sample to small test tube of hard glass and anneal in vacuo for several hours at 450°. This process frees any CO or CO_2 which may be present.

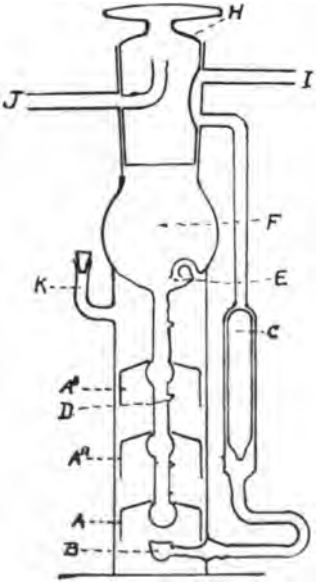

FIG. 2. Potash Bulb.

A dozen samples can be conveniently treated at the same time by putting them into a pyrex tube two feet (60 cm.) long by one inch (2.5 cm.) in diameter, which is wound with 25 ft. (7.5 m.) of nichrome ribbon $\frac{1}{16}$ in. (1.5 mm.) wide (resistance per ft. (30 cm.) is 1.2 ohms) and is connected to the 110 volt lighting circuit. The nichrome may be wound directly upon the glass. Radiation is cut down by two layers of asbestos tape, wound over

the nichrome. A slightly inclined position of the heating tube prevents spilling of the open sample from test tube containers. After annealing the samples, they are cooled, removed and stoppered till ready for use. Samples furnished by the Bureau of Standards contain very little external or occluded carbon and may be used for standardization without annealing.

Absorption of CO_2—New Potash Bulb.

It is imperative that the CO_2 from the process of combustion be adsorbed quantitatively. Several potash bulbs were used, but due to incomplete absorption, fragility, difficulty in manipulation, etc., a new bulb was made which has proven to be useful and very efficient.

The potash bulb, see Fig. 2, may be described as follows: Gas is introduced through *I*, passes through the valve *C*, and is emitted at *B*, through a multiple of fine openings which break the gas up into fine bubbles. The gas is next caught in the movable cup *A*, which soon fills. The gas is momentarily retarded in its upward path through the solution by the weight of the cup. When nearly filled with gas the cup lifts vertically and the gas is emptied into *A*, as the lower cup reaches the constricted portion of the supporting rod. The little glass peg prevents the cup from sticking should the gas flow become too rapid. The trapped gas having escaped, the cup drops and is immediately filled with the inflow of gas. Cups *A*, *A'* and *A''* work similarly. By retardation of the gas in its upward movement by the cups which are constantly wet with solution, by holding the gas at a slightly increased pressure momentarily, excellent absorption takes place. The gas then enters the P_2O_5 chamber *F* through the orifice *E*, where any vapor from the absorbing liquid is caught. The stopper *H* may be turned, closing off the inlet *I* and outlet *J*. The inlet *K* is used for filling the lower chamber and is closed with a small rubber stopper. The apparatus is compact, light and is easily handled, thus minimizing weighing errors. A comparatively large amount of liquid may be used in the bulb, thus giving sufficient solvent for many runs, which at the same time assures complete solution of the gas.

Table I gives the results of first trial with the absorption bulb in the usual combustion train. Later results, where special precaution in procedure was taken, show values invariably a few thousandths higher than the certificate value.

TABLE I.

Results of Bureau of Standards Samples.

Sample	*Certificate Value	Value Found
B. O. H. 0.1% C No. 15 a	0.111	0.110
Vanadium Steel No. 24.	0.348	†0.342
Chrome Tungsten No. 31.	0.599	0.604
Chrome Nickel No. 32.	0.383	0.391
Nickel Steel No. 33.	0.278	0.281

*Average of all methods.
†No fluxing oxides used at 1050° C. Result probably low.

Furnaces Used for Combustion of Ferro-Alloys.

To insure complete combustion of the sample, working temperatures up to 1500° C. were desired. This was facilitated by the use of three combustion furnaces, namely a granular carbon resistance furnace, a platinum furnace and a nichrome furnace of the general type designed by Dr. Yensen. The carbon resistance furnace could be easily heated to 1500° C., but due to diffusion of carbon through the silica tube only a few runs could be made with the same silica as the combustion tube. Several protective coatings were used outside the silica tube, such as fire clay, alundum and mixtures of these with sil-o-cel and asbestos. All materially lengthened the life of the silica tube but in no case at this temperature did the carbon fail to penetrate through the coating. Otherwise this type of furnace is very desirable because of its simplicity of design and range of temperature. An alundum tube inside of which, and fitting closely, is placed a silica tube,

serves very well for a protective sleeve for the silica combustion tube. The platinum furnace, made by the Stupakoff Laboratories, could be used safely to 1450° C., the fusing point of magnetic iron oxide. The nichrome furnace was used almost entirely to 1100° C., and served very well for this purpose, and may be briefly described as follows:

Nichrome Furnace. The accompanying diagram (Fig. 1) shows the construction of the combustion furnace. The outer casing *I* of the sheet metal is in the form of a 10 in. (25 cm.) tube and is 20 in. (50 cm.) long. The ends *H* and *F* are made of transite boards, the one of shorter diameter just fitting inside the metal

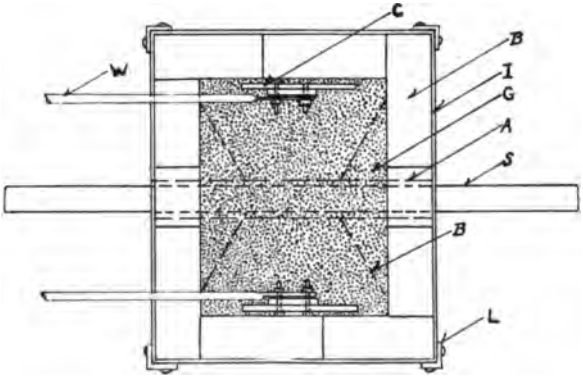

FIG. 3. Carbon Resistance Furnace. Diagram of Top View.

casing. A hole of such diameter as to accommodate the alundum sleeve *J* is cut into *F*. The packing and heat insulator *K*, surrounding *J* and inside, is filled before securely bolting the body together by means of the rods G. A silica tube, used as the combustion tube, is wound with ⅜ in. (9 mm.) x 0.003 in (0.075 mm.) nichrome ribbon, the portions of the tube near the end having the winding slightly crowded to maintain a more uniform temperature along the combustion tube. The winding is held in position by asbestos tape *D*, and clamped into position by the metal band *E*. A winding may be replaced in 10 minutes. One winding will last for many combustions if the furnace is not crowded to its maximum working range of 1200° C. A copper tube *A*, ⅛ in. (3 mm.) diameter, is wound about the end of the silica tube. Circulating

water through *A* keeps the ends of the combustion tube cool so that rubber stoppers may be used without danger of contamination of carbon.

Carbon Resistance Furnace. Fig. 3 is a diagram of the top view of the Hill furnace and Fig. 4 is the vertical view. A sheet metal casing 13.5 in. (34 cm.) x 7 in. (18 cm.) is supported by angle iron legs *L*. The furnace is lined on the bottom by fire brick and on the sides by sil-o-cel brick *B*. An alundum tube *A*, or other sleeve material is supported by the sil-o-cel brick so that the combustion tube *S* is easily slipped into position. The electrodes *C* are made of carbon, the tops being copper-plated to prevent oxidation at the lead-carbon junction. To protect the part

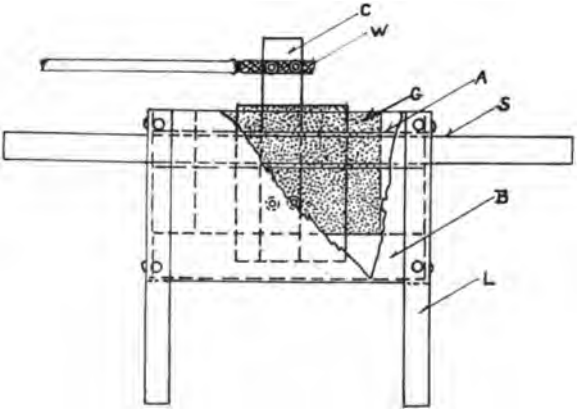

FIG. 4. Vertical View of Carbon Resistance Furnace.

just below the lead, the electrode is given a coating of sodium silicate. The central chamber is packed with fine granular carbon, the wedge-shaped sil-o-cel construction *G* suffices to concentrate the heating at the central part of the combustion tube. The furnace may be quickly brought up to working temperature. The input at 1500° C. is about ½ kilowatt.

Accuracy of Results.

Special care must be taken at all points of the carbon determination to insure the best results. The plus and minus errors are nearly divided, so that the average result, though relative, is nearly correct. However, the usual combustion results are some-

what low. *Errors that are additive:* Poor purifying train, presence of external C, diffusion of carbon through silica tube at high heat, heating of stoppered ends of tube, and the presence of Cl, SO_2, H_2O, etc., at the point of absorption. *Subtractive errors:* Leaks in system, incomplete or rapid fusion of sample, escape of C as CO, presence of incombustible material as carbides, lack of proper oxides to fuse sample, occluded CO or CO_2, and incomplete absorption of CO_2 in bulb. Weighing errors may be plus or minus. Temperature of combustion is important. In the presence of an oxide, as PbO or Fe_2O_3, carbon is eliminated slowly at temperatures as low as 300° C. A run of 24 hours made upon Armco iron at 500° C. gave 0.027 percent carbon, whereas the total carbon contained in the sample was 0.033 percent. At temperatures around 1000° C. the elimination of C is very rapid under oxidizing conditions. Runs were made up to 1450°; no advantage is gained where the combustion is carried out above 1100° C.

Table II gives the results of carbon analyses on iron-carbon alloys. These results are representative of many analyses made on the other alloys.

TABLE II.

Sample Marked	Carbon Content by Weight	Difference from Mean	Average Carbon Percent
2-204 C	0.0005 0.0006	±0.0001	0.019
2-C-201	0.0012 0.0012	±0.0001	0.041
2-114-F	0.0011 0.0010	±0.0001	0.035
2-C-202	0.0016 0.0016	±0.0001	0.058
2-201 X	0.0012 0.0007	±0.0003	0.031
2-C-205	0.0046 0.0048	±0.0001	0.157
2-C-204	0.0047 0.0048	±0.0001	0.158
2-218	0.0014 0.0010 0.0009	+0.0003 —0.0001 —0.0002	0.032

Summary.

1. A new absorption bulb of high efficiency has been described.

2. Carbon content of ferro-alloys probably determined to ± 0.002 percent.

3. Slow diffusion of carbon takes place well below ordinary temperature of combustion under oxidizing conditions, but process is too slow for combustion work.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

THE MANUFACTURE OF FERRO-ALLOYS IN THE ELECTRIC FURNACE [1]

By C. B. Gibson.[2]

The demand for ferro-alloys is governed, to a large extent, by the requirements of the iron and steel industry. As specifications for ordinary, tool and alloy steels, and also castings, are becoming more rigid, the steel maker is depending on ferro-alloys to meet these requirements.

Prior to about 1890 ferro-alloys were made in the blast furnace or crucible, and to a limited degree in the open hearth. However, each of these methods had its limitations. The blast furnace temperatures were insufficient for the reduction of certain oxides of the alloying metals, and the large quantity of carbon charged did not permit of making alloys low in carbon.

The crucible method was limited by the restricted output on a tonnage basis and lack of sufficient temperature to melt the alloys and reduce the oxides.

Accordingly, the introduction of the electric furnace in 1890, based on the researches of Moissan, for the production of ferro-alloys, was the active beginning of the ferro-alloy industry on a commercial scale.

A ferro-alloy is an alloy of iron and some other metal. It is used by the steel maker as a cleansing and deoxidizing agent, the alloy combining with the oxygen or other impurities and passing off in the slag, or for introducing into the steel a certain percentage of the alloying metal to give the steel certain physical properties, depending on the alloy used.

The alloys in general use for deoxidizing are ferro-manganese, ferro-silicon, etc. The alloys used for imparting to steel certain properties are ferro-manganese, ferro-chromium, ferro-tungsten, ferro-molybdenum, ferro-vanadium, ferro-uranium, ferro-titanium, ferro-zirconium, etc.

[1] Manuscript received February 8, 1920.

[2] Westinghouse Electric and Manufacturing Co., East Pittsburgh.

Ferro-manganese, in addition to its deoxidizing property, imparts to steel certain physical qualities. When added in amounts of 12 to 14 percent it makes steel hard and tough. More ferro-manganese is made than any other alloy. Most of it is produced in the blast furnace, although some is being made in the electric furnace. The loss of manganese in the slag is approximately 5 to 15 percent less with the electric process than with the blast furnace, but against this saving is the increased cost of electric power and the smaller scale of operation for the electric process. The raw materials are manganese ore, carbon, a small amount of silica and iron. While figures are not readily available as to the comparison of the two methods, it is hoped this comparison will be favorable to the electric process.

The expansion in ferro-silicon during the past few years has been on a large scale and there are a number of plants producing this alloy. The raw materials charged are ordinary silica and iron turnings or punchings. Ferro-silicon has a great affinity for dissolved oxygen, and is about four times as active as manganese in removing oxygen. Silicon steel is used almost entirely for transformer punchings on account of its low hysteresis and high permeability.

Ferro-chromium (often improperly called ferro-chrome) follows ferro-silicon in amount produced. The raw materials are chromite and carbon. When added to steel it imparts an extreme hardness, and the steel is used for armor plate, gears, cutting tools, etc. Steel with 10 to 12 percent chromium is non-tarnishable and is used in making cutlery and surgical instruments, being sold as "stainless steel."

Ferro-tungsten also imparts to steel an extreme hardness, and machine tools containing a certain percentage of ferro-tungsten can be run at a red heat without, in any way, impairing their hardness. Tungsten steels have contributed materially in increasing the output and production of numerous plants, due to the more rapid rate at which drilling and machining operations can be done. For electrical contacts, pure tungsten has practically superseded the use of platinum. The raw materials are either black oxide of iron or a white oxide of calcium and tungsten (calcium tungstate). Ferro-tungsten is also sold under the name of ferro-wolfram.

Ferro-molybdenum added to steel imparts characteristics somewhat similar to ferro-tungsten. The raw materials are molybdenite (MoS_2) concentrates, carbon, iron scrap or turnings, and an excess of lime, which are charged in the electric furnace. If the percentage of molybdenum does not exceed 50 to 60 percent, the alloy can be tapped, but above this percentage, on account of the higher melting point, it cannot be tapped and the furnace is allowed to cool and then dismantled in order to remove the alloy.

Ferro-vanadium imparts to the steel the property to resist shock and vibration, and such steels are used for axles, cranks, connecting rods, etc. Vanadium is obtained from the radium ores of Colorado.

Ferro-uranium also imparts to steel strength and resistance to shock.

Ferro-titanium is used to remove gases, such as oxygen and nitrogen, from steel. The raw materials charged are a double oxide of titanium and iron (titanic iron ore).

The success of any ferro-alloy plant is dependent on several factors. (1) The proper design of furnace, accessories, and electrical equipment. (2) A thorough knowledge of the metallurgical problems. (3) Low power rates, and advantageous location of plant with respect to labor, raw materials, freight facilities and market.

The general design of electric furnaces for producing alloys is much the same, but differ in the electrical connections, the number and arrangement of electrodes, and the shape and size of the hearth. Furnaces are either single, two, or three phase.

The single-phase furnace is arranged for either one or two electrodes. The Siemens is an example of the former type. Here the current enters one vertical electrode which is suspended in the furnace directly above the hearth. The furnace is lined with a refractory material and carbon, which is connected to the returning conductor of the circuit. The furnace shell is usually round. A tap hole is provided at the lower side. The electrode is raised or lowered by hand or a motor-operated winch connected to the electrode by a cable. This type is sometimes referred to as a pot furnace, and is employed in the production of ferro-tungsten and molybdenum. If the alloys cannot be tapped the furnace can be knocked down and the alloy button removed.

The single-phase furnace is also built using two electrodes, and the current which enters one electrode passes through the charge and out the other electrode. The shell is similar to the Siemens furnace, although it is usually rectangular. It is built with open or closed top. The latter is used with metals of high-melting point in order to conserve the heat.

The three-phase furnace is used almost entirely for producing ferro-manganese, ferro-silicon, and ferro-chromium. The shell is either rectangular or oval, lined with a refractory material and the bottom with carbon. The bottom shell is either air or water cooled, and the tap hole is provided at the lower side. The open top permits continuous charging of the furnace, and while the volatilization losses are greater, this loss is compensated for by the greater ease of operation and handling of the furnace.

As to the most suitable size of furnace, this is dependent on the kind and character of alloy produced. Small single-phase furnaces lend themselves most suitably for such alloys as cannot be tapped and require taking the furnace apart in order to remove the alloy. For alloys which can be tapped and for which there is a larger tonnage demand, these are made in the large open top furnaces, as this type is more efficient. Also, the operating costs in labor and attendance are less.

The proper design of a furnace is dependent on several factors. (1) There must be a proper relation of the essential parts of the furnace. (2) The character of the charge and the magnitude of the electrical parts, which are factors in producing heat and causing the chemical reactions and smelting of the materials, must be carefully considered. (3) The size and shape of shell, size and relative location of electrode, and amount of power output, all influence to a greater or lesser degree the results obtainable.

The question of single- *vs.* three-phase furnaces is influenced by the power requirements. A single-phase load often causes considerable unbalancing to a three-phase line, which is usually objectionable to the central station company. This objection is often overcome by connecting a number of single-phase furnaces to the three phases and distributing the load as evenly as possible. With such an arrangement, it is the aim to have several furnaces operating so as to give more nearly balanced conditions. The three-phase furnace is the most desirable from the standpoint of balanced load.

The power consumption of a furnace for different alloys is dependent on the size of the furnace, the proper handling of the charge and operations, and on the percentage of alloy being produced. Tables Nos. I and II give the approximate KW. days per ton of alloy produced.

TABLE I.

Power Consumption and Raw Materials for Some Ferro-Alloys. (E. F. Cote.)

Product	Per Ton of Manufactured Product		
	KW.-Day (24 Hrs.)	Raw Material Handled Tons	Tons Raw Material Handled per KW. Year
Ferro-Silicon, 50 percent.....	300	3.0	3.3
Ferro-Silicon, 80 percent.....	650	4.0	2.0
Ferro-Chromium, 8 percent.....	360	4.0	3.7
Ferro-Molybdenum	360	3.5	3.2
Ferro-Tungsten	325	3.0	3.0

TABLE II.

Prof. Georges Flussin Gives the Following Data:

Product	Per Ton Manufactured Product		
	KW.-Day (24 Hrs.)	Raw Material Handled Tons	Tons Raw Material Handled per KW. Year
Ferro-Silicon, 10 - 12 percent.....	109	1.55	4.7
" " 25 - 30 percent.....	172	1.90	3.65
" " 45 - 50 percent.....	333	2.90	2.87
" " 70 - 80 percent.....	714	4.30	1.99
" " 90 - 95 percent.....	1000	6.40	2.11
Ferro-Manganese, 18 - 20 percent.....	67	1.80	8.85
" " 70 - 75 percent.....	167	3.15	6.23
Ferro-Chromium, 10 percent C.....	286	2.97	3.34
" " 1 percent C.....	555	4.05	2.41
Ferro-Tungsten	286 to 400	2.70	3.11 to 2.23
Silico-Manganese, 10 percent Si - 20 percent Mn.....	133	2.20	5.46
Silico-Manganese, 10 percent Si - 70 percent Mn.....	217	2.50	3.80
Silico-Manganese, 25 percent Si - 50 percent Mn.....	333	2.70	2.69

TABLE III.

R. H. Keeney Gives the Following Figures on the KW. Hours per Pound for Certain Ferro-Alloys.

Product	Size Furnace		Type	Percent Recovery	KW. Hrs. Per Lb. Alloy Tapped
	Tons Charged	Kilo-watts			
Ferro-Silicon, 50-70 percent.	3-4	1000	1-Ph.	....	2.5-3
Ferro-Manganese, 75-80 percent Mn.....	15	1200	3-Ph.	70-85	2.2-3.3
Ferro-Chromium, 60-65 percent Cr, 4-6 percent C....	13-15	750	3-Ph.	70-80	3-4.5
Ferro-Tungsten, 70-75 percent W.....	0.75	150	1-Ph.	80-90	2.1 Sm't. 1.7 Ref.
Ferro-Molybdenum, 60-65 percent Mn., 15-20 percent C.....	....	150	1-Ph.	78-80	7-7.5*
Ferro-Vanadium, 30-35 percent. V, 3-4 percent Si.....	1	150	3-Ph.	75 Av.	3.4
Ferro-Uranium, 35-50 percent U., 3-4 percent C....	800 lbs.	75	1-Ph.	75	3.5

* Per lb. of Mo in alloy.

The above values give a fairly close check on the power requirements, materials charged and tonnage output for the more common ferro-alloys. The amount of electrical energy required per ton of output may be calculated theoretically. It is first necessary to determine the heat necessary to bring the charge to the temperature at which the reaction takes place and the energy absorbed by such reactions, and add to this the losses in radiation, conduction, and in the gases given off, also the electrical losses in electrodes, and circuit and deduct from this the heat developed in the furnace by the chemical reactions. Knowing the amount of the charge, the specific heats, the latent heats, and the physical characteristics of the furnace, these calculations can be made.

In addition to a properly designed furnace, there are several other equally important considerations, such as furnace voltage, type of electrode holder and method of cooling, facilities for charging and tapping, suitable refractories, arrangement of winch mechanism, etc.

Equally important as the furnace is the proper selection and design of the electrical equipment. The electrical equipment for

a ferro-alloy furnace comprises (1) incoming line protective equipment; (2) furnace transformers; (3) motors for operating the winches for raising and lowering the furnace electrodes; (4) automatic regulators for maintaining constant current at the furnace, and (5) switchboard panel, including instruments, circuit breakers, relays, etc.

The protective equipment, such as lightning arresters, choke coils, and disconnecting switches, also the switchboard panels are usually of standard construction, and it is only necessary to make the proper selection of apparatus to meet the existing conditions. One of the most important points is to make sure that the main circuit-breaker is of sufficient size and rupturing capacity to open the furnace circuit with the power concentrated behind it. In a large number of installations, especially those using hydro-electric power, there are many thousands of horsepower feeding directly into the line.

Direct-current winch motors for driving the winches are generally used, although alternating current is used in a few cases. The motors if installed in the furnace room are totally enclosed to protect them from the dust and dirt usually present. In the more recent installations, the winch and motor are located in the transformer room and connected with the electrode by means of a cable supported on pulleys.

In selecting a winch it is necessary to know the weight to be lifted and the speed of the electrode travel, and the manner of fastening the cable.

The proper selection of furnace transformers is one of the most important considerations on account of the unusually severe operating conditions of a furnace load. The transformer should be designed to withstand properly and effectively the stresses which are set up within it due to surges and short circuits caused by the electrodes coming in contact with the charge. In the smaller sizes the bracing problem is not as important but for transformers feeding furnaces of 5,000 to 20,000 horsepower and with large energy capacity behind the line, this is a more difficult problem. Fortunately, transformers are and can be designed and built to meet fully these conditions.

Since the average furnace voltage is comparatively low for the transformer capacity, the low-tension winding is of few turns of

large cross section and the leads are of still larger section. The coils and leads must be so arranged, spaced and interlaced as to give a balanced design. Since transformers can be designed to withstand effectively and satisfactorily momentary short circuits, from this standpoint it is unnecessary to provide high internal reactance in the transformer. The low-voltage leads of small transformers usually consist of flat copper bus, drilled and spaced to facilitate connecting to the bus bars running to the furnace.

Another important consideration is the question of ventilation of the furnace transformer. Due to the heavy secondary current and rather severe overloads occurring, the copper coils and iron core must be properly ventilated in order to give uniform heating with absence from hot spots in the transformer.

The furnace voltage required for smelting ferro-alloys usually ranges between 50 and 100 volts. The most suitable voltage depends on the general furnace layout. Provision is often made in the transformer for several different low voltages, which is an advantage where different alloys are made in the same furnace at different times.

The general tendency is to work a furnace just as hard as possible, as regards the KV.A. input, with the view of increasing the tonnage output and of decreasing the smelting period, thereby effecting certain economies in operation. There are, however, conditions which limit the amount of power which can be fed into a furnace. Among these conditions is the voltage of the service and the currents involved, the inductance of the circuit, as determined by the form and dimensions of the circuit and frequency, skin effect as determined by the shape and size of conductor section. The reduction of self-induction and skin effect are two of the most important considerations. They are reduced by laminating the individual conductors of the proper size and shape and by interlacing the conductors.

In laying out new furnace installations, or in planning to improve the operating conditions of existing ones, a careful study is essential of the problems relating to the bus and cable layout. Relatively the problems involved in 25-cycle installations, for the same size furnace, are not as serious as for 60-cycle, for the reason that maximum energy that can be fed into a constant voltage circuit at different frequencies is inversely proportional to

the frequency. In other words, where a 10,000 horsepower, 60-cycle furnace is about the limiting size for a well-designed furnace and bus layout, 22,000 horsepower is the corresponding size for a 25-cycle furnace.

It is sometimes advantageous to feed more power into a furnace during certain periods. This is possible by using a higher impressed voltage, since the power input to a circuit of given frequency is proportional to the square of the impressed voltage.

Of the more recent developments in electric furnace equipment, undoubtedly the greatest improvements have been in those devices for automatically controlling the current input to furnaces by a movement of the electrodes. While it has been generally recognized, in the past, that automatic regulation, as compared with manual operation, effects a large saving in labor charges, more efficiently utilizes the electrical power and reduces materially the time required for a charge, these new devices embody many improved features of interest to the furnace operator. These features permit of much higher speeds of electrode travel, eliminate all over-travel or pumping of the furnace electrodes on melting, and of arcing at regulator contacts, also prevent any electrode feeding down into the molten bath.

The entire ferro-alloy field is one of absorbing interest. The possession of large supplies of alloys was one of the important features in winning the war, as alloys were indispensable to the steel industry. Undoubtedly, new alloys and new uses for those now available, or combination of alloys, will be found, and we can confidently expect this industry to keep pace with the steel industry in meeting the present and future demands.

DISCUSSION.

COLIN G. FINK[1]: The author has said that ten thousand horsepower is the limit on a 60-cycle furnace, and twenty-two thousand on a 25-cycle furnace. I should like to ask him which is going to win out? That is, is the advantage of the larger furnace going to more than make up the difference in the lower frequency?

C. B. GIBSON: That is a point upon which there seems to be quite a difference of opinion among the ferro-alloy manufacturers.

For a while the tendency seemed to be toward larger furnaces for the manufacture of ferro-silicon, ferro-chromium and ferro-manganese. I have heard some authorities on ferro-silicon say that they think about three thousand kilowatts is the most suitable commercial size furnace, when considered from all standpoints. Also I have heard of others who are considering five and ten thousand kilowatt furnaces. My opinion is that the relative efficiency of the different sizes is not fully known at the present time and it is to be hoped that sufficient data will be published to definitely establish these facts. As the other alloys are made usually in small furnaces they would not be considered. For furnaces for the manufacture of carbide the tendency is to go to the largest sizes possible.

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RECENT DEVELOPMENTS IN THE FERRO-ALLOY INDUSTRY.[1]

By Robert J. Anderson.[2]

Abstract.

A discussion of conditions in the ferro-alloy industry, particularly during the last five years, and particularly in reference to the relations of the industry in the United States to that in foreign countries. The recent progress in the metallurgy of the ferro-alloys is discussed in detail for each of the alloys, including the minor ferro-alloys and those of complex composition. The present status of the electric furnace production of ferro-alloys in the United States is next considered, together with factors affecting the domestic ferro-alloy industry, such as the supply of metallurgical ores, electric power and the location of ferro-alloy plants, and the trade situation. [J. W. R.]

The striking developments of the past five years centered the world's ferro-alloy industry in the United States, and this country was the foremost producer of practically all kinds of ferro-alloys in 1918. Prior to the war, ferro-alloys were not produced in the United States in large tonnages with the exception of ferro-manganese, spiegeleisen and blast-furnace ferro-silicon, and the electric furnace output of the other steel-making alloys was very small. This abrupt change in our position as referred to that of France, Germany, and England, was engendered by conditions growing out of the war, and it was principally due to the greatly increased demand for all kinds of ferro-alloys used in the production of simple-carbon and special steels, as well as to the high prices which ruled. The output and consumption of ferro-alloys

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in the world is closely connected with the rise and fall in the steel trade, and the greatly increased output of steel ingots and special steels of all kinds for particular purposes during the war reflected favorably on the ferro-alloy industry. During the past five years, the ferro-alloy industry in the United States has been characterized as follows: (1) the rapid increase in output of all kinds of ferro-alloys until 1919, accompanied by some new departures in metallurgical practice which are worthy of note; (2) the liquidation and collapse in 1919; and (3) tariff agitation.

The outstanding features of the metallurgical (ferro-alloy) ore industry have been practically identical. Prior to the war, France was the pioneer and leader in ferro-alloy metallurgy and output of special steel-making alloys, particularly ferro-alloys made in the electric furnace, and French alloys were introduced and used in every steel-making centre of the world through the efforts of Girod and others. Great Britain dominated the ferro-manganese markets, and independent steel makers in the United States were largely dependent upon British ferro-manganese. The United States Steel Corporation produced the bulk of its own requirements but it was not a seller of this alloy for either domestic or foreign consumption. Spiegeleisen requirements of the American steel industry were supplied practically entirely by domestic merchant and other stacks, and some spiegeleisen was exported.

Although Germany occupied a far less important position than France, the former had complete control of the world's tungsten markets, as regards tungsten ores and concentrates, ferro-tungsten, and tungsten powder. Germany was a large buyer of tungsten ores in the principal mining centers of the world and had a firm foothold in South America; Germany, incidentally, secured a large amount of the British controlled Burma output, as well as ores from the United States, Portugal, and Bolivia. Germany reduced tungsten ores and manufactured tungsten powder and ferro-tungsten which were shipped to all steel-making centres, but Germany did not make much tool steel, nor did she use much tool steel. Both Great Britain and the United States shipped tungsten ores and concentrates to Germany for reduction into tungsten powder and ferro-tungsten, and these latter products were then imported from Germany. The importance of tungsten was thoroughly realized by Germany, but neither the United States nor

Great Britain had adequately appreciated the value of tungsten-ore supplies until the war commenced. When the war started, tungsten (and tungsten-bearing materials) was the second article placed on the embargo list by Great Britain.

The situation in the United States as to the other ferro-alloys, prior to the war, was generally the same as in the case of ferro-tungsten, but the importance of tungsten naturally overshadowed the other alloys. Exceptions may be made, however, as to the ferro-titanium alloys and ferro-vanadium, because the United States had long been an important producer of these alloys for domestic consumption, but not largely for export. Before the war, it had long been realized by many people that the position of the United States in the ferro-alloy industry of the world was distinctly anomalous when considered in relation to the domestic steel industry. The greatest steel industry in the world has been within the confines of the United States for many years, but this country was not an important factor in the production of ferro-alloys, particularly as regards electric-furnace alloys.

In regard to electric-furnace ferro-alloys, practically all kinds were made in the United States prior to the war, but the development of the electric-furnace manufacture in this country had been slow compared to Europe.[3] There were definite reasons for the backward condition in the United States, of which high power costs was the dominating one. However, embargoes by foreign countries, high prices, and the strong demand during 1915-1918 stimulated production here as never before; the necessary incentive to undertake ferro-alloy manufacture was supplied, and existing plants were enlarged and many new companies entered the field.

The ferro-alloy industry, both blast furnace and electric furnace, reached its highest development when hostilities ceased; the demand was then suddenly withdrawn, and the industry faced the problems of readjustment to peace conditions. Readjustment problems have been pressing in other industries also, but they have been especially momentous in the ferro-alloy industry because the domestic expansion and development occurred in such a short period of time. The motor industry, for example, changed from

[3] Lyon, D. A., Keeney, R. M., and Cullen, J. F.: The electric furnace in metallurgical work, Bureau of Mines (1916), Bull. 77, 105-106.

a war to a peace basis in three months, but the ferro-alloy industry has scarcely yet been readjusted. Whereas in 1918 the electro-metallurgical plants were operating at more than rated capacity and additions and extensions were planned, in 1919 some of the branches of the industry had declined to pre-war levels and others had collapsed entirely. The collapse was brought about by the sudden withdrawal of the demand, by the necessity for liquidation of large overstocks left in buyers' hands, and by large foreign offerings as well as dumpings of ferro-alloys.

It has been previously indicated that the mining of metallurgical ores is closely connected with the ferro-alloy industry, and the problems which were faced by ferro-alloy makers in 1919 have been truly reflected in the plight of the miners. Monetary relief has been provided for the compensation of mining operators of chromium, manganese, and tungsten mines through the War Minerals Relief Act, but no particular relief has been afforded the ferro-alloy makers. The alarming decline of the industry in both mining and smelting has resulted in much agitation for the enactment of protective tariffs which will allow the average-cost operators to continue in business. More regarding this will be said later.

In dealing with the recent developments (1913-1920), it is advisable to consider both metallurgical and trade progress, as well as the several factors which affect the ferro-alloy industry in this country. The technical developments in the production of metallurgical ferro-alloys in the United States prior to the war were the result of gradual betterments in existing practice, but since 1915 some new departures have been introduced; certain of these have been only temporary, but others, it is believed, will prove permanent. Among the latter may be mentioned the electric furnace production of ferro-manganese and low-grade ferro-silicon. The trade development and output of ferro-alloys have been briefly touched upon, and this aspect of the industry will be more fully considered in later paragraphs.

When the attempt is made to forecast the future of the domestic ferro-alloy industry, numerous difficulties are presented, and in fact the future of some branches is more dependent upon tariff legislation than upon any other one factor. Moreover, it is necessary to deal with each individual alloy separately because the

governing factors affecting each are different in distinct particulars. The object of the present paper is to point out the recent important developments which have occurred in recent years, to indicate the status of the industry today, and also to show what may reasonably be expected in the future under certain conditions.

Recent Progress in the Metallurgy of the Ferro-Alloys.

In dealing with progress in the metallurgy of the ferro-alloys, it would also be advisable ordinarily to deal with technical advances in the mining of metallurgical ores, concentration and chemical recovery, as well as developments in the metallurgy of ordinary and tool steels. Any attempt to do this would make the paper too long, but any cognate matter will be touched upon briefly. Recent progress in the metallurgy of the ferro-alloys has been characterized by some important departures from pre-war standard practice in this country, as well as by numerous technical and scientific investigations looking to the more economical manufacture and utilization of steel-making alloys. Much attention has been given to mining and concentration problems for the purpose of securing better recoveries and preventing waste, and these investigations should prove to be of substantial value to the industry and the country. The government technical and scientific investigations were confined principally to manganese[4] and tungsten to a lesser extent, but chromium, vanadium, and other metals would have been studied at length had the war lasted longer.

The ferro-alloy industry is relatively old, having been built up with the steel industry, but the significant metallurgical advances have come since 1899 with the employment of the electric furnace for the manufacture of all kinds of ferro-alloys. Ferro-manga-

[4] U. S. Bureau of Mines, War Minerals Investigations Series Bulletins, as follows:
Christianson, P., and Hunter, W. H., The Jones process for concentrating manganese ores: Bull. No. 12, March, 1919.
Crane, W. R., Preparation of manganese ore: Bull. No. 17, May, 1919.
Gillett, H. W., and Williams, C. E., Electric smelting of domestic manganese ores: Bull. No. 10, December, 1918.
Hoyt, S. L., The use of manganese alloys in open-hearth steel practice: Bull No. 11, December, 1918.
Newton, E., Problems involved in the concentration and utilization of domestic low-grade manganese ores: Bull. No. 9, December, 1918.
Royster, P. H., Production of ferro-manganese in blast furnaces: Bull. No. 5, December, 1918.
Royster, P. H., Production of spiegeleisen in blast furnaces: Bull. No. 6, December, 1918.
Weld, C. M., Review of the manganese situation: Bull. No. 7, December, 1918.
Weld, C. M., and Crane, W. R., Cost of producing ferro-grade manganese ores: Bull. No. 13, March, 1919.

nese, spiegeleisen, and low-grade (Bessemer) ferro-silicon are still produced mainly in the blast furnace, but crucible practice for the manufacture of other principal ferro-alloys has vanished. At the present time, ferro-chromium, ferro-tungsten, ferro-titanium, ferro-molybdenum, and ferro-uranium are made principally in the electric furnace and a subordinate amount of some of these by the thermit process; ferro-vanadium is made largely by a modification of the thermit process in an open-hearth furnace, but the electric furnace has been gaining ground for ferro-vanadium reduction. The electric-furnace manufacture of ferro-silicon has grown to large proportions, and this alloy is made in all grades in the electric furnace. Generally speaking, the thermit alloys are higher in price than electric-furnace alloys, and they are subject to the market fluctuations in the price of aluminum while the latter are not. Metallurgical progress and tendencies are discussed briefly below for each individual alloy.

Ferro-Manganese and Spiegeleisen.—A great deal of attention was given to manganese during the war, and several metallurgical changes in practice were put into effect. The standard contents of ferro-manganese (78-82 percent) and of spiegeleisen (18-22 percent) were lowered to 70 and 16 percent manganese respectively, so as to make practical the utilization of lean domestic ores, and to conserve manganese. At the same time, two other alloys, silico-manganese[5] and silico-spiegel, came into some prominence. In the conservation efforts carried out during the war, it was shown that the lower grades of ferro-manganese and spiegeleisen could be satisfactorily employed in steel making, but the personal prejudice of most steel makers is against such alloys; immediately after the restrictions were removed at the close of the war, production of the lower grade alloys ceased, and the former standard grades are now made exclusively. Efforts were also made to substitute spiegeleisen for ferro-manganese for the higher carbon steels; this was not a metallurgical advance, but rather a retrogression to the practice of the Bessemer rail mills, using cupolas to melt the spiegeleisen. An investigation carried out with the idea of conserving manganese in open-hearth practice[6] and utilizing alloys other than ferro-manganese, pointed out

[5] Swann, T., The development of the ferro-manganese industry in the United States since 1914: Chem. and Met. Eng. (1918), 19, 672.
[6] Hoyt, S. L., work cited.

metallurgical advances in three directions, *viz.*, (1) the use of a molten spiegel mixture for deoxidation and recarburization; (2) the practice of melting and refining the steel bath so as to insure a relatively high residual content of manganese; and (3) the use of manganese alloys containing silicon (silico-manganese). As has been mentioned, the use of silico-manganese and silico-spiegel was extended somewhat. Difficulty in obtaining sufficient supplies of ore suitable for the production of ferro-manganese led to active consideration and large scale experiments in the smelting of manganese-lean and siliceous ores in the electric furnace for making so-called intermediate alloys such as the following:

Alloy	Approximate Chemical Composition, Percent			
	Mn	Fe	Si	C
Silico-manganese	55-70	20-5	25	0.35
Silico-spiegel	20-50	67-43	4-10	1.5-3.5

Alloys like the above can be made readily in the electric furnace, but the extent to which they can be employed depends largely upon the prejudice of the American steel maker rather than upon metallurgical considerations. It has been demonstrated, however, that large tonnages of silico-manganese can be used in the United States in the manufacture of steels to which both ferro-manganese and ferro-silicon must normally be added, and sufficient evidence is at hand (based on foreign practice as well as large scale experiments in this country) to indicate that the use of silico-manganese is metallurgically sound and desirable.[7] Prior to the war, practically all the ferro-manganese made in the United States and elsewhere was a blast-furnace product, and a metallurgical development of importance has been the commercial electric-furnace manufacture of this alloy. No spiegeleisen has been made in the electric furnace as a commercial alloy, and the entire output is made in the blast furnace. Scarcity of ferro-manganese, high prices of coke, and shortage of ores made it profitable for a number of electric-furnace plants to be built for the production of ferro-manganese, and it was generally found advantageous to

[7] Gillett, H. W., and Williams, C. E., work cited.

build them near manganese mines, even in the face of high power costs.

During the period when the electric-furnace ferro-manganese plants were developed in the United States, many of the difficulties incident to reduction of the alloy were overcome, but metallurgical progress is still possible in several directions, *viz.*, as to size of units, voltage to be employed, and reduction of losses by dusting and in the slag. Any decided metallurgical progress in ferro-manganese smelting by the electric furnace is doubtful, for it is problematical whether any more than a very few of the more advantageously situated plants can continue operations under present conditions. Both fuel and manganese losses in the blast-furnace production of ferro-manganese are normally high,[8] manganese losses varying from 15 to 25 percent in the slag, whereas in electric-furnace practice this loss has been brought down to 10 percent. Until the latter practice becomes more firmly established, metallurgical developments of signal importance can be readily effected in blast-furnace practice, notably by the use of low-ash coke and low-silica stone[9] and large savings can be made by adherence to metallurgical principles in the operation of manganese-alloy stacks.

Manganese recovery in the manufacture of silico-manganese by the electric furnace is, however, normally quite high (about 95 percent) because of the absence of slag, and the direct manufacture of silico-manganese is a marked advance over the earlier method employed of mixing molten ferro-manganese and ferro-silicon to form the desired alloy. Ordinarily, blast furnaces making ferro-manganese can operate economically on ores containing not much less than 40 percent (or 35 percent at least) Mn, nor more than 12 percent Si, but the electric smelting of both low-grade domestic ores and manganiferous slags has been shown[10] to be metallurgically feasible; it is scarcely profitable to attempt to so smelt such ores in normal times and prices.

The Jones (direct reduction) process for the concentration of manganese in manganiferous iron ores, where the association of the manganese and iron is so intimate that the ordinary gravity- or magnetic-separation methods fail, has been shown to be metal-

[8] Richards, J. W., The ferro-alloys: Chem. and Met. Eng. (1918), 19, 501-504.
[9] Royster, P. H., work cited.
[10] Gillett, H. W., and Williams, C. E., work cited.

lurgically sound, but its possibilities under normal conditions in the ferro-manganese industry are not yet proved. Looking back over the metallurgical developments of the past five years in ferro-manganese and related alloys, it is seen that numerous investigations have pointed the way to advanced practice, and, although some of the experiments made have not been demonstrated commercially under normal conditions, the general progress has been of significant importance. It is unfortunate that the same cannot be said of some of the other alloys which, metallurgically, stand in about the same position as they did ten years ago.

Ferro-Silicons.—From the standpoint of tonnage produced, ferro-silicon is the most extensively used of all the ferro-alloys made in the electric furnace. Blast-furnace ferro-silicon, so-called Bessemer grade, had been manufactured for many years in the United States, but there were only one or two producers of 50 percent electric-furnace ferro-silicon in this country prior to 1914. Owing to the large demand in the steel industry, the number of producers was increased to about 15 in 1918, but during the period of liquidation and collapse in 1919 a number of the plants have been dismantled and junked.

The main reason for the slow development of electric-furnace manufacture of ferro-silicon in the United States had been the cost of power; power consumption is normally very heavy, and although the cost of raw materials is low, it had previously been found cheaper to import 50 percent alloy, as well as the higher grades. Steadily increasing open-hearth capacity prior to the war caused a regular increased consumption of 50 percent ferro-silicon, but this was not reflected in further expansion of the domestic output to any extent. The great expansion in the domestic output of ferro-silicons of all grades, as well as that of Canada, England, and France, was the result of the enormous quantities of shell and munitions steel made; these steels run fairly high in silicon, considerably higher than ordinary structural steels, and large amounts of ferro-silicon were required.

A number of new electric-furnace plants were installed during the period 1914-1918, most of the expansion coming during the first three years of the war, with Canada taking an advanced position. The higher grades of ferro-silicon, containing 75 and

90 percent Si, found increased application in the manufacture of high-silicon electrical steels, and the manufacture of these alloys was undertaken by steel companies for their own consumption.

No important metallurgical advances have taken place in blast-furnace ferro-silicon practice, but the production of low-grade ferro-silicon (10-15 percent Si) in the electric furnace is worthy of note. Whether the electric-furnace producers of low-grade ferro-silicon can compete with the blast-furnace makers is somewhat conjectural, but the former have made a determined attempt in 1919 to establish themselves in this field. Only the lowest grades of ferro-silicon can be made in the blast furnace because of the difficulty of reducing silica, and all the higher grades must be made in the electric furnace; there have been some attempts, however, to produce 50 percent ferro-silicon in the blast furnace by using a blast enriched with oxygen.

The over-expansion of electric-furnace capacity for ferro-silicon during the war period was markedly shown by the collapse in 1919. Although ferro-silicon is normally produced in electric furnaces only in localities where power is cheap, under the conditions brought about by the war, the higher grade alloys were manufactured profitably even where power is relatively dear, for example at Baltimore, Md., near Pittsburgh, Pa., and at Anniston, Alabama.

Ferro-Chromium.—This alloy, usually and erroneously called ferro-chrome, is an electric-furnace product almost exclusively; a carbon-free grade is made by the thermit process. Prior to the introduction of the electric furnace for ferro-alloy manufacture, practically all ferro-chromium was made in the blast furnace; a small amount was made in the crucible. Only low-tenor ferro-chromium can be made in the blast furnace, and then, for alloys containing about 40 percent Cr, rich ores, high temperatures, and high blast pressures are required; coke consumption is also normally excessive. The older methods have been practically superseded because of the distinct advantages offered by the electric furnace, but the demands of the steel makers for high-tenor ferro-chromium low in carbon have been an additional incentive to electric-furnace manufacture.

There were only two domestic makers of ferro-chromium prior

to the war, but the number of producers in 1918 was about ten, and the capacity was about 25,000 tons per annum. The situation in ferro-chromium has been somewhat analogous to that in ferro-tungsten, but the metallurgical advances in ferro-chromium have been more noteworthy in the past five years. Metallurgical progress has been made in the direct production of low-carbon ferro-chromium in the electric furnace, in the refining of high-carbon alloys, and in smelting lean domestic ores. Keeney's notable experiments on the smelting of low-grade ores and chromium slags[11] have contributed materially to recent metallurgical progress. It has now been shown that good recoveries of chromium may be expected when smelting lean ores provided the carbon in the resultant alloy is allowed to run high enough (7 percent); from a metallurgical standpoint, entirely satisfactory results have been obtained from high-grade domestic ores in smelting all grades of ferro-chromium.

During the war, most of the ferro-chromium used in the steel industry was for the manufacture of chromium-nickel and chromium-vanadium steels, either directly or indirectly for government requirements, but with the withdrawal of the war-demand some of the new companies, which made ferro-chromium, have been forced to suspend operations temporarily or completely. The alloy containing 6-8 percent C and 60-70 percent Cr is a standard grade, but some steel makers prefer high-tenor alloys with less carbon. The metallurgical difficulties in making a low-carbon alloy require further investigation, for at the present time the cost of additional refining makes the cost of low-carbon alloys several times as much as high-carbon ones.

Ferro-Tungsten.—Prior to 1914, nearly all of the tungsten powder and ferro-tungsten used in the United States for the manufacture of high-speed steel was imported from Germany, but during the war the United States became a large producer and exporter of ferro-tungsten and metallic tungsten. The metallurgical importance of tungsten is due practically entirely to its use in the manufacture of high-speed steel, and about 95 percent of all the tungsten (whether as concentrates, ferro-tungsten, or tungsten powder) produced or imported, ultimately finds its way

[11] Keeney, R. M., The manufacture of ferro-alloys in the electric furnace: Bull. A. I. M. E., Aug., 1918, pp. 1321-1373.

into special steels. Some people entertain the idea that much tungsten is employed in tungsten-lamp manufacture, but the amount used for that purpose is infinitesimal compared to the total quantity consumed.

The growth of the manufacture of ferro-tungsten and tungsten powder in the United States is best shown by the following: prior to 1914, practically no ferro-tungsten was made here, although at the same time Germany was importing ores from this country and shipping ferro-tungsten for American consumption. At the close of 1918, there were about 20 domestic makers of ferro-tungsten and tungsten powder, but some of these have been obliged to cease operations in 1919. Normal consumption of 60 percent WO_3 concentrates for the manufacture of ferro-tungsten and tungsten powder is now rated at about 7,500 tons per annum, by a leading maker.

Naturally, during the war the demand for tungsten for high-speed steel to be used in machining shells, munitions, and machinery was enormous, but in normal times the demand had expanded heavily with the development of the automobile. A further increased demand is looked for in connection with tractor development, which promises to be very large, and the demand for high-speed steel is certain to advance. The metallurgical advances in the manufacture of ferro-tungsten have been few in recent years, and the main technical progress in the tungsten industry of the United States has been in connection with milling and concentration; at the height of the tungsten-ore production, the milling of ores in Boulder, Colo., district had reached the highest development[12] anywhere in the world.

Formerly, tungsten powder was used almost entirely for fixed additions to steel, but the powder has now been replaced to a considerable extent by low-carbon 80 percent ferro-tungsten. At the present time, in the manufacture of high-speed steel about 50 percent of the tungsten used is in the form of ferro-tungsten, the remainder being tungsten powder. Metallurgically, there should be no particular advantage in either, but if the ferro-tungsten is not homogeneous variations in the tungsten content of the steel may occur. On the other hand, loss by oxidation in

[12] Fischer, S., Modern concentration of Colorado tungsten ores: Met. and Chem. Eng. (1917), 16, 559-565; and *idem.* (1917), 17, 73-78.

making fixed additions to steel are claimed to be less when ferro-tungsten is employed than tungsten powder. The use of ferro-tungsten is growing in favor. No serious difficulties are met with in the reduction of ferro-tungsten in the electric furnace; it is one of the easiest alloys to reduce and does not so readily oxidize or form carbides as chromium and uranium. No progress has been made in tapping high-grade ferro-tungsten from the electric-furnace, and the alloy is still made principally in knock-down furnaces. Lower grade ferro-tungsten can be tapped, but it is not practice to do so. The ability of domestic makers to turn out a high-tenor, uniform, ferro-tungsten has been demonstrated, and the use of tungsten powder is likely to decrease, more ferro-tungsten being made from year to year. Some ferro-tungsten is still made by the reduction of tungsten concentrates in the crucible with carbon, but the bulk of the output in the United States is made in the electric furnace by reduction with coke or other form of carbon.

Ferro-Vanadium.—About 75 percent of the ferro-vanadium made in the United States is manufactured by the thermit process, or by a modification of the thermit process in the open-hearth furnace using metallic aluminum as the reducing agent. The remainder of the ferro-vanadium is made in the electric furnace using 90 percent silicon as the reducing agent. Consequently, the price of ferro-vanadium is affected largely by the fluctuations in the aluminum market and to a less extent by the price of silicon. Reduction of vanadium oxide or vanadate of iron by carbon in the electric furnace has been generally abandoned because of the difficulty in holding carbon low in the resultant ferro-vanadium, and this element is highly objectionable to steel makers.

Metallurgical advances in ferro-vanadium as to the thermit reduction of the alloy have been almost at a standstill, and the main technical advances have come in the chemical processes for extraction of vanadium from domestic ores, particularly the Colorado carnotite,[18] in the development of vanadium steels for castings and forgings, and in the use of vanadium in high-speed steels. The 33 percent ferro-vanadium has been shown to be the most suitable for use in the metallurgy of steel. Silicon metal

[18] Moore, R. B., and Kithel, K. L., Uranium, radium, and vanadium: Bureau of Mines, Bull. (1914), 70.

has been found to be the most satisfactory reducing agent for electric-furnace practice, but high-grade ferro-silicon can also be used. Metallurgical progress has been made in the refining of high silicon ferro-vanadium so as to obtain a product containing less than 1 percent Si, and it is much easier to reduce the silicon content of ferro-vanadium by refining than the carbon content of the same alloy made by reduction with carbon.

In connection with the recent reorganization of the American Vanadium Co., plans called for an electric-furnace installation for working over the large slag dumps at Bridgeville, Pa., for the purpose of recovering the vanadium lost by the earlier operations. Additional progress has been made in metallurgical investigations looking to the utilization of domestic ores, particularly the vanadinites and complex ores of New Mexico and Arizona.[14] With the threatened decline in the output of the Peruvian mines, the domestic vanadium-bearing minerals of little importance at present may become commercial ores of vanadium.

A noteworthy change in recent years has been the introduction of vanadium into high-speed steels, particularly all high tungsten-chromium and molybdenum-chromium steels. The growth of the ferro-vanadium branch of the ferro-alloy industry in this country has not been so marked in the last five years as was the case with ferro-silicon, ferro-tungsten, and ferro-chromium; however, the United States was the largest maker of ferro-vanadium both before and during the war, and the domestic output increased considerably during the war period. There were two or three domestic producers of ferro-vanadium prior to 1914 and six or seven at the close of 1918.

Ferro-Titanium Alloys.—Alloys of iron and titanium were developed for use in the metallurgy of steel after the introduction of the electric furnace, and at the present time the greater part of the ferro-titanium made in the United States is an electric-furnace product. Some carbon-free ferro-titanium is made by the thermit process, but this alloy also contains varying amounts of aluminum. There are still two distinct kinds of ferro-titanium alloys manufactured, one called ferrocarbon-titanium, containing

[14] Conley, J. E., Treatment of cuprodescloizite for extraction and recovery of vanadium, lead and copper: Chem. and Met. Eng. (1919), 20, 465-469; and, A proposed metallurgical process for the treatment of vanadinite for the recovery of lead and vanadium, *idem.*, 514-518.

15-18 percent Ti and about 6 percent C, and the other a carbon-free product, containing about 25 percent Ti. The former is made in the electric furnace and the latter by the thermit process.

The use of titanium-treated rails fell off markedly for several years prior to 1914 because of the ascendency of the open-hearth process in making rail steel; consequently with the decline of Bessemer tonnage of rails, the amount of ferro-titanium alloys used in their manufacture decreased rapidly. This followed because it was thought that the supposed superiority of the open-hearth rail would obviate the use of titanium in rail steel, but further experience indicated that the use of ferro-titanium alloys was also desirable for open-hearth rail and other steels, so that titanium is again used in large amounts for scavenging steel. About 2,500,000 tons of steel were treated with ferro-titanium alloys in 1918, and the metallurgical value of additions of titanium has been shown to be of distinct importance in treating all kinds of steels.

During the war, in connection with conservation of manganese, numerous experiments were carried out for the purpose of substituting ferro-titanium alloys for ferro-manganese either in whole or in part; partial substitution of ferro-titanium for ferro-manganese has been successfully effected, and this practice will probably continue to increase in view of the results obtained on a large scale. One steel plant has been able to reduce the usual amount of ferro-manganese about 50 percent by addition of ferro-titanium in the ladle. No important metallurgical advances[15] in the smelting of ferro-titanium have occurred, and although numerous patents have been taken out in recent years for metallurgical improvements and new methods, the recent progress has been largely the result of gradual betterments in previously existing practice. Exports of ferro-titanium alloys have continued to grow, and the United States continues to occupy a leading position in the titanium branch of the ferro-alloy industry.

Ferro-Molybdenum.—This alloy has suffered some peculiar vicissitudes in fortune from the metallurgical standpoint, and an exceedingly large amount of contradictory information has been issued in regard to the value and properties of molybdenum

[15] Anderson, R. J., The metallurgy of titanium: Journ. Frankl. Inst. (1917), 184, 469-508, 637-650, 885-900.

steels. However, the employment of molybdenum in the metallurgy of steel is admittedly in its infancy, and too much cannot be logically expected at the present time. Prior to 1914, only about 10 tons of ferro-molybdenum[16] was made annually in the United States and that almost entirely for export. Ferro-molybdenum is now generally made in the electric furnace directly from raw molybdenite (MoS_2) concentrates, although it was formerly made by the reduction of the roasted sulphide in the crucible with carbon as the reducing agent. At the present time, the use of roasted ore has passed, and the molybdenum-bearing material for reduction with ferro-molybdenum may be raw molybdenite concentrates, or a sodium molybdate (Na_2MoO_4) slag obtained from wulfenite.

Experimental runs have been made in Canada with pure molybdic acid.[17] In the electric furnace either carbon or silicon metal is used as the reducing agent; the former is more generally employed, and the use of silicon (and ferro-silicon for the production of the lower grades of ferro-molybdenum) is a recent commercial departure, although covered by early patents. In 1918, several hundred tons of ferro-molybdenum were produced in the United States, largely for export, and during the war period Canada became a large producer of the alloy. Even yet, because of the infancy of the industry, standard grades of ferro-molybdenum are not well established,[18] but alloys are offered containing from 50 to 80 percent Mo and 1 to 3 percent C. As in the case of ferro-tungsten and ferro-chromium, metallurgical advances in the smelting of ferro-molybdenum have not been marked in recent years, and the technical developments in the molybdenum industry have come largely in the concentration of molybdenite by flotation and in the development of molybdenum steels. Molybdenite concentration[19] had reached a high state of development in the United States and Canada in 1918, but the collapse of the molybdenum market has compelled domestic mines and mills to suspend operations.

The development of molybdenum steels has been the result

[16] Keeney, R. M., work cited.

[17] Parsons, A. L., Molybdenite deposits of Ontario: 26th Ann. Rept. Ontario Bureau of Mines (1917), 26, 275-313.

[18] Anderson, R. J., Ferro-alloys in 1918: Eng. and Min. Journ. (1918), 107, 83-86.

[19] Horton, F. W., Molybdenum; its ores and their concentration: Bureau of Mines, (1916), Bull. 111.

of European investigations principally, and further application of these steels is looked for. Considerable furore has been raised recently over the molybdenum steel developed by Dr. Arnold in England, but this development, in fact, dates back to 1899 and essentially calls for the use of vanadium and the substitution of molybdenum for tungsten. Much of the actual development in molybdenum steels during the war was closely connected with ordnance matters both here and abroad, and the results of experiments are just now coming out. Among other things, the development of complex molybdenum steels for forgings is noted, as well as the use of calcium molybdate for making fixed additions of molybdenum to steels. There is an ample supply of workable ore in the United States, notably the deposit at Climax, Colo., and this country should have no difficulty in supplying its own internal requirements of ferro-molybdenum. In the past there has been doubt as to whether supplies of ore would be available, but with that doubt definitely set out of the way, the expansion of the domestic ferro-molybdenum industry rests solely on the future of molybdenum steels.

Ferro-Uranium.—This is one of the more recent ferro-alloys to be suggested and used in the metallurgy of steel, particularly for fixed additions in the manufacture of so-called uranium tool steels. All of the ferro-uranium made in the United States for commercial sale is obtained by reduction of by-products derived from the carnotite ores of Colorado, secured principally by the method of extraction employed by the National Radium Institute.[20] The important metallurgical advances in ferro-uranium and uranium steels have dated from the original work of the Bureau of Mines in co-operation with the Institute and a private steel company; ferro-uranium was developed principally to secure an outlet for the large amounts of sodium uranate, $Na_2U_2O_7$, which accumulated as a by-product from radium production.[21] Sodium uranate is converted into the black oxide of uranium by reduction with carbonaceous material on fusion with sodium-chloride, and the resulting uranium oxide, UO_2, is the raw material for the electric-furnace production of ferro-uranium.

[20] Parsons, C. L., Moore, R. B., Lind, S. C., and Schaefer, O. C., Extraction and recovery of radium, uranium, and vanadium from carnotite: Bureau of Mines (1915), Bull. 104.

[21] Keeney, R. M., work cited.

The general method developed for the manufacture of ferro-uranium of varying grades is by reduction of uranium oxide with carbon in a tilting electric furnace; ferro-uranium cannot be economically made by the use of silicon metal as a reducing agent because the recovery is low and the silicon content of the resulting alloy too high. It has been shown that ferro-uranium containing from 40 to 70 percent U and about 2 percent C can be made commercially, without a second refining operation, under certain conditions,[22] and refining for lowering carbon in the case of ferro-uranium is undesirable because of the tendency of the alloy to lose uranium by oxidation into the slag. From the metallurgical standpoint it is difficult to make a low-carbon ferro-uranium simply by regulating the amount of carbon charged, as is the case with some of the ferro-alloys.

Some further experiments have been made in recent years on the production of metallic uranium, as well as in the use of metallic uranium for fixed additions to steel. Metallic uranium (containing considerable uranium carbide) has been made by the reduction of uranium oxide with petroleum coke in a stationary electric furnace, but the direct recovery of uranium is low. Furthermore, uranium metal is not so satisfactory as ferro-uranium for making fixed additions to steel because of its high melting point and ease of oxidation. Ferro-uranium has been shown to be the more suitable, and the grade containing about 25 to 35 percent U is satisfactory when less than 2 percent U is required in the resultant steel.

Minor and Complex Ferro-Alloys.—Numerous alloys of iron with other elements have been suggested and used in the metallurgy of steel for various purposes, including ferro-aluminum, ferro-boron, ferro-cerium, ferro-cobalt, ferro-nickel, ferro-phosphorus, ferro-tantalum, ferro-zinc, ferro-zirconium, ferro-silico-aluminum, ferro-manganese-aluminum, ferro-silico-manganese-aluminum, ferro-calcium-silicide, ferro-titanium-aluminum-silicide,[23] and some others. Ferro-aluminum is not being made, but an important metallurgical possibility for its manufacture from ferruginous bauxite in the electric furnace is suggested by

[22] Gillett, H. W., and Mack, E. L., Preparation of ferro-uranium: Bureau of Mines (1917), Tech. Paper 177.

[23] Anderson, R. J., Ferro-manganese in the iron and steel industry: Journ. Frankl. Inst. (1917), 183, 587.

Richards.[24] It was formerly made as a regular alloy for the final deoxidation of steel, but its use ceased when commercial aluminum became relatively inexpensive. As an electric-furnace alloy made from bauxite, it probably can be made to sell at a less relative cost than aluminum.

The electric-furnace work to date on ferro-boron has been largely experimental, *i. e.,* ferro-boron has been made for determining the effect of additions of boron to steel, but no alloy maker in the United States has yet undertaken its manufacture on a commercial scale. The alloy is made in the electric furnace by the direct reduction of colemanite with iron ore and carbon. Ferro-cerium is one of the newest of the ferro-alloys; it is made by the direct alloying of iron with misch-metal (50-60 percent Ce, 25 percent La, 15 percent Di, Sa, etc., and 1-2 percent Fe), and the ordinary ferro-cerium contains 30 percent Fe and 70 percent misch-metal.

Considerable experimental work has been carried out on cerium steels during the past five years, but the results of the majority of these investigations have not been made public. Ferro-cerium has recently been employed as a deoxidizer for cast iron,[25] where it has been found to increase the transverse strength and deflection. Its deoxidizing action is excellent because of the high heats of oxidation of the cerium-group metals. Ferro-cobalt is not made any longer, so far as is known, but a number of patents pertaining to complex ferro-cobalts and other cobalt alloys have been secured.[26] Cobalt metal is preferred to ferro-cobalt for making fixed additions in the manufacture of cobalt-bearing tool steels, but the use of cobalt in these steels is declining. Ferro-nickel is seldom made in the electric furnace, but usually by the direct alloying of iron and nickel in the desired proportions; however, nickel is added to steel usually as metallic nickel rather than as ferro-nickel. Ferro-phosphorus is an important steel-making alloy, but the tonnage consumed is not large; it is employed for making fixed additions of phosphorus in the open-hearth in the manufacture of sheet steels.

Ferro-phosphorus is made in the United States in the electric

[24] Richards, J. W., work cited.

[25] Moldenke, R., Cerium in cast iron, abstd. Iron Age (1920), 105, 324-325.

[26] Drury, C. W., Cobalt, its occurrence, metallurgy, uses, and alloys: Rept. Ontario Bureau of Mines (1918), 27, part 3, section 1.

furnace and in the blast furnace, by reduction of apatite and phosphate rock, and the electric-furnace manufacture of this alloy, in connection with the fertilizer industry is a development which occurred during the war period. Domestic consumption of ferro-phosphorus has been steadily increasing because of the increased demand for automobile sheets, and the electric-furnace manufacture of the alloy has been undertaken by several companies in the United States in the past few years. Ferro-zirconium is one of the newest of the ferro-alloys; it is used for the manufacture of special zirconium steels. The alloy has been made by the thermit process, but its regular manufacture has not been undertaken commercially in the United States.

Further interest has been shown in ferro-silico-aluminum during the past two years, and experiments on the use of the alloy as a deoxidizer for steel are now being carried out; it has been recently made in the electric furnace at Baltimore, Md. A large number of patents have been secured for the preparation of numerous complex ferro-alloys, but most of these alloys have not been applied on a working scale in the metallurgy of steel.

Present Status of the Electric-Furnace Production of Ferro-Alloys in the United States.

This section of the paper will point out the present status of the electric furnace manufacture of ferro-alloys in the United States, and the various factors which affect the ferro-alloy industry will be taken up later. The development of the metallurgical ferro-alloys for use in steel practice has progressed with the development of the electric furnace, and it is not possible to produce the majority of the ferro-alloys of commercially required quality without this appliance. Exceptions to this are seen in blast-furnace ferro-manganese and spiegeleisen, blast furnace ferro-silicon, and thermit ferro-vanadium. From a metallurgical standpoint, the main problem involved in the production of commercial ferro-alloys has been the manufacture of high tenor alloys, low in carbon and other impurities (chiefly phosphorus and sulphur) undesirable in steel.

The quality of the ferro-alloys made has been largely dictated by the steel maker, but it has not always been possible for ferro-alloy makers to supply the exact alloy wanted. It is desired that

ferro-alloys for steel metallurgy shall have reasonably low melting points so that they can be readily incorporated into the ordinary steel bath without the necessity of superheating the steel, and that they shall be homogeneous. The developments of the past five years in the United States show that the electric furnace is becoming an important factor in the production of ferro-alloys previously made mainly in the blast furnace, for example ferro-manganese, low-grade ferro-silicon, and ferro-phosphorus, and the manufacture of electric-furnace ferro-vanadium has gained ground.

Ferro-manganese is now an electric-furnace alloy, 15 percent of the total domestic output being made electrically in 1918, but the greater part of the output will continue to be made in the blast furnace. Silico-manganese is now a regular commercial electric-furnace alloy, and low grade iron-manganese alloys have been made electrically. Because of the savings of fuel and manganese, electric-furnace ferro-manganese will continue to be made in localities favored by high-grade ore and nearby hydro-electric power at reasonably low rates.

Ferro-silicon of various grades is now regularly made in the electric furnace in the United States, and the electric furnace ferro-silicon plant has its choice of a wide range of alloys to manufacture. Normally, the alloys made in the blast furnace are low-silicon alloys, known as Bessemer ferro-silicons, and the standard grades contain 10, 11 and 12 percent Si. All other ferro-silicons, 50, 75, 80, and 90 percent grades, are made in the electric furnace; the lower grades containing 10-15 percent Si have also been regularly made in the electric furnace during the past few years. The latter have doubtless come to stay, and it appears that this alloy has held its own even in the late unsettled markets. The electric-furnace production of ferro-silicon has grown to large proportions, but the location of plants in the United States has been confined in the main to localities where electric power is relatively cheap, as at Niagara Falls, N. Y., and Keokuk, Iowa; the large consumption of power in the reduction of ferro-silicon is the main item of cost, but plants have been operated at points where electric power is relatively dear, as at Baltimore, Md., Anniston, Ala., and near Pittsburgh, Pa.

Ferro-chromium is manufactured in greater tonnage by the electric furnace than any other ferro-alloy except ferro-silicon, and the capacity of the existing plants in 1918 was placed at 25,000 tons per annum; accurate statistics are not available. The passing of the blast furnace for reduction of ferro-chromium and the demands of steel makers for fairly low-carbon alloys high in chromium have firmly established the electric furnace in this branch of ferro-alloy manufacture. Some chromium metal and carbon-free ferro-chromium is made by the thermit process, but these materials cannot compete on a price basis with electric furnace ferro-chromium. Expansion in electric-furnace manufacture of ferro-tungsten in the United States has been most remarkable during the past five years, particularly in the western states of Colorado, California, and Washington; some of the new companies have dropped out during the period of liquidation in 1919 but the majority of them have continued to make ferro-tungsten even in the face of foreign dumping.

The manufacture of ferro-tungsten in this country is firmly established, and provided sufficient supplies of ore can be obtained the majority of the ferro-tungsten makers will apparently be able to continue operations, tariff or no tariff. Ferro-vanadium manufacture in the electric furnace has gained ground, although the thermit process still contributes the greater part of the domestic output; this is because most of the production is made by one company using the thermit method, but the tendency toward electric-furnace manufacture is strong. Ferro-molybdenum is exclusively an electric-furnace alloy; it is made in the usual ferro-alloy plant having an output of various kinds of alloys. Electric-furnace ferro-titanium (high in carbon) is the principal iron-titanium alloy made, but the carbon-free product is still produced in fairly large amounts. Ferro-uranium is an electric-furnace alloy exclusively, but most of the ferro-zirconium has been made by the thermit process. The mode of manufacture of the minor alloys has been indicated already, but it is well to again mention the increasing use of the electric furnace for the production of ferro-phosphorus, and the experiments with electric-furnace ferro-silico-aluminum.

In viewing the present status of the electric-furnace manufacture of the principal ferro-alloys, the United States stands in a very strong position as compared to its pre-war status, both as to

metallurgy and output. Significant advances have been made, but the idea is prevalent that these may be allowed to languish because of inability of many of the new companies to continue operating. It is certain that with the war demand withdrawn and foreign competition again active, as well as with a return to normal conditions, many new companies cannot continue in ferro-alloy manufacture, and the future has been largely discounted by the readjustments in 1919. However, the technical advances in metallurgy will be applied by companies which do continue to operate, and the experiments of the war period will point the way to less costly future progress.

Metallurgically, and from the standpoint of output, more has been accomplished in ferro-alloy manufacture during the period 1914-1918 than in the 20 years preceding the war. There is no reason to fear for the technical standing of the United States in the metallurgy of the ferro-alloys. When attempting to forecast the immediate future outlook for the industry in the light of recent developments, it is, however, necessary to consider a number of factors which affect the production of ferro-alloys in this country; chief among these are ore supplies, foreign competition, and power costs.

Factors Affecting the Ferro-Alloy Industry in the United States.

The future of the domestic ferro-alloy industry is somewhat conjectural at the present time, particularly as regards ferro-chromium and ferro-tungsten, as well as ferro-silicon, because of tariff agitation, and the uncertain industrial outlook. There has been witnessed a remarkable development in the United States during the period 1914-1918 in the production of all kinds of ferro-alloys, until the world's industry was centered here rather than in France; during 1919, the industry largely collapsed because of definite causes already discussed.

Generally speaking, the ferro-alloy industry may be said to follow the rise and fall in the steel trade, but it is not advisable to take this generality too literally. The readjustments during 1919 have shown, however, that the domestic industry is not at all likely to decline permanently to pre-war levels, but will continue to hold the greater part of its gain acquired during the war period. The more important factors affecting ferro-alloy manufacture in

the United States include costs and supplies of metallurgical ores, quality of ores, freight rates on ores and alloys, location of ores in respect to location of hydro-electric power sites, cost of electric power and coke (anthracite coal and charcoal), costs and supplies of refractories and fluxes, demands of the steel makers as to quality of ferro-alloys, tariffs and the trade situation, steel output, development and use of special and high-speed steels, and several other items. Some of these items are discussed below and others will be touched upon briefly.

Supply of Metallurgical Ores.—The United States is not internally independent for its supply of metallurgical ores for ferro-alloy manufacture, despite the fact that some misleading statements to the contrary have appeared. Moreover, in the case of particular ores such as chromium and tungsten ores, although this country can supply its own internal requirements in emergencies, it is not economically possible to do so in normal times because of the strong competition with cheap foreign ores. It is more precise to say, however, that the strong competition existing among ore miners for the domestic market is rather more among foreign producers than between domestic mines and foreign ones. Unassailable statistics and cost figures have shown that the domestic miner of metallurgical ores of chromium, tungsten, and manganese cannot attempt to compete with the cheap and high-grade foreign ores, which can be laid down at Atlantic ports even against high ocean-freight rates at much lower prices than must be paid for lower grade domestic ores f. o. b. mines.

With exception of the period during the recent war, this country has been quite largely dependent upon foreign ores for many years, and it will continue to be so dependent, in the opinion of the domestic ore producers, unless suitable protection is given so that the domestic miners can operate their mines. The Timberlake and Kahn bills, designed to protect the tungsten and chromium interests of the country, may be cited in connection with tariff regulations now pending which vitally concern ore producers, ferro-alloy makers, and steel manufacturers, and ultimately the consuming public. The outcome of the legislation proposed and pending is somewhat doubtful, but constructive legislation is expected to insure the future of the domestic ferro-alloy industry in all its branches.

In regard to manganese ores, it is believed that some of the large domestic mines may be able to continue operating, tariff or no tariff, but such mines, as in the past, must be high-grade and favorably located with respect to the market. Thus, the Arkansas, Virginia, California, and possibly Montana mines will continue to be worked for supplies of manganese ore for ferro-alloy manufacture, but the great bulk of the ore supplies for ferro-manganese must continue to come from Brazil and India, and Russia, if the latter ever gets on a rational basis again. The bulk of the manganese ore must continue to come from foreign sources, because domestic ores of the required grade are not existent in sufficient quantity.

The operation of electric-furnace plants near domestic mines will tend to increase, provided hydro-electric power is available nearby and the mine is not too far from the market for ferro-alloys. The largest Pacific-coast alloy makers, for example, can doubtless continue to make ferro-alloys, but ferro-alloy manufacture in Montana even from nearby ores and with fairly cheap hydro-electric power is not an economic possibility at the present time. Where there is a fairly high-grade manganese mine, near the steel making centre of the United States, as at Neva, Tenn., it will probably be profitable to operate an electric-furnace plant for the production of ferro-manganese near the mine and ship the alloy. The ore situation in manganese markedly affects the manufacture of ferro-manganese and spiegeleisen in the United States, particularly as to location of plants.

The situation as to available domestic supplies of tungsten ores is one which is so intimately linked with costs and foreign competition that a word of explanation is necessary. Incidentally, it may be said that no branch of the ferro-alloy industry is in greater need of stabilization than tungsten. Large supplies of tungsten ores are available in the Atolia, Calif., and Boulder, Colo., fields, and the newly opened Nevada district is promising; the surface deposits of exceptional richness in the first two fields are exhausted and deep mining is now required for removing the ore.

However, under an *ad valorem* tariff of 10 percent on tungsten-bearing ore, American mines must practically suspend operations in a $17 ore market, South American mines must stop production

at $11-$12 a unit, but Chinese ore can still be shipped at $7 a unit (now that Chinese provincial taxes on tungsten ore have been removed). This simply means that the question of price, and price alone, determines where the domestic ferro-tungsten maker obtains his ore. Some qualification of the statement just made is necessary; for example, some grades of Chinese ore containing tin, bismuth, and copper are objectionable, and these ores are penalized because of the smelting difficulties. Even under the proposed Timberlake bill, over half of the tungsten-ore supplies for the domestic manufacture of ferro-tungsten and tungsten powder must continue to be drawn from foreign sources.

In the matter of chromium ores, the situation is somewhat analogous to that of tungsten, although even under the prices and demand, restriction of imports, scarcity of ocean bottoms, and high ocean-freight rates, more than one-half of the chromite and chromiferous-iron ore consumed in the United States in 1918 came from distant foreign sources, principally New Caledonia, Rhodesia, and Brazil. The bulk of the metallurgical ore for the manufacture of ferro-chromium must continue to come from foreign sources, tariff or no tariff, but reasonable protection, such as suggested in the Kahn bill, will provide for the average-cost mines operating in competition for the domestic market with New Caledonia and Rhodesia.

There is an abundance of molybdenum ore in the United States, the developments at Climax, Colo., being especially noteworthy; all the domestic requirements for metallurgical ore for the production of ferro-molybdenum can be readily taken care of by the Colorado mines. The ore supplies available are more than sufficient to provide for any demand now discernible, for 30 years, and output is solely dependent upon the developments which may occur in molybdenum steels. Ordinarily, not much ilmenite or titaniferous iron ore is produced in the United States, and the supplies required are imported; the domestic resources are, however, large.

A new development calculated to increase the domestic output of rutile and ilmenite (as well as zircon and monazite) is the new milling plant at Pablo Beach, Fla., which is operating on local complex monazite sands. The output of rutile by the Virginia

mines is, however, usually in excess of the demand. Ample supplies of silica for ferro-silicon or siliceous iron ores, are available, and the cost of raw materials for the manufacture of ferro-silicon is normally low; ferro-silicon makers at times feel the pinch of the iron-scrap markets, but there is no difficulty in obtaining sufficient silica.

Vanadium ores for the manufacture of ferro-vanadium still continue to be drawn largely from Peru, and unless the demand for ferro-vanadium increases markedly, there is little prospect that the vanadinites of New Mexico and Arizona can contribute supplies; decline of the Peruvian ore reserves may increase the use of domestic ores. Ferro-vanadium is also made, however, from the by-products of radium extraction, and the carnotite ore of Colorado is the chief domestic source of supply of vanadium. Most of the zirconium ore used to date has come from Brazil, but there is the possibility that the recent Florida developments may be able to supply part of the zirconium requirements of the country. Ample supplies of domestic ores are available for the production of ferro-aluminum, ferro-boron, and ferro-phosphorus, in the event that any demand appears for the first two, while the abundant phosphate rock of Tennessee and other southern states can supply all discernible demands for ferro-phosphorus.

Electric Power and the Location of Ferro-Alloy Plants.—The cost and availability of electric power for electro-metallurgical work is a determining factor in the location of ferro-alloy plants as well as in the choice of process employed for some alloys. The domestic ferro-alloy industry has been centered for years near sources of relatively cheap power, *viz.*, Niagara Falls and the Pacific coast, largely in the former place, but with the advent of outrageous prices during the war it was profitable to operate plants at points where power was relatively costly and far removed from the steel-making centers. Foreign ferro-alloy progress has largely followed the hydro-electric developments in France, Switzerland, Italy, Norway, and Sweden, and the domestic ferro-alloy industry did not expand at the same rate as the foreign industry prior to the war because of lack of cheap power and the remoteness of cheap power where it might have been made available. This is a condition which will not be soon overcome in the United States,

and ferro-alloys plants will continue to be located chiefly according to the relative weight of these factors: (1) cost and availability of power; (2) location of hydro-electric plant; (3) distance to steel-making centers; (4) location of high-grade ore supplies. The first three factors are the predominating ones under normal conditions, but emergencies such as a war can radically upset accepted practice. Thus, with prices sufficiently high, it has been profitable to use relatively costly electric power for the manufacture of ferro-manganese rather than to employ the blast furnace and coke as a fuel; high coke prices and heavy demand coupled with high prices made the electric-furnace manufacture of ferro-manganese economically possible even in districts remote from the ferro-manganese markets.

The Trade Situation.—The trade situation in metallurgical ores and ferro-alloys is closely linked with the matter of protective tariffs, but small *ad valorem* tariffs as embodied in the Payne and Underwood bills had no practical effect on the international markets. The present and recent demoralized exchange rates have proven to be the most disconcerting of tariffs, because with a premium on dollars and a discount on francs, pounds, marks and lire, the foreigner is anxious to sell here and buy elsewhere. Thus, in 1919 it was thought that much of the overstock of ferro-alloys held in the United States could be disposed of to satisfy the presumed pent-up foreign demand, but under offerings of foreign alloys at prices below even the domestic re-sale market such hopes quickly faded. There were also abnormally heavy overstocks of ferro-alloys on hand in foreign countries when the war ended, and these overstocks both here and abroad caused a temporary flooding of the markets. The result was an extremely confused market[27] in 1919, which was dominated by re-sales, dumping of foreign alloys, and even exports of some domestic alloys (particularly spiegeleisen) against ridiculous exchange values.

Without going into the exchange situation at length, it can be readily seen that foreign business in ferro-alloys cannot be booked for large tonnages under present conditions, and the foreign countries must trade among themselves. To consider a specific example; depressed exchange rates are more favorable to

[27] Anderson, R. J., The ferro-alloy industry in 1919: Eng. and Min. Journ. (1920) 109, 204-208.

England than to the United States because the former country can secure and keep all the European trade she can care for, so long as the British pound costs less in Paris or Berlin than the American dollar. (No consideration is here given to long term credits or actual barter).

It has been previously pointed out that the domestic consumption is closely linked with the rise and fall in the steel trade, and development in the ferro-alloy industry closely follows development in the steel industry. Unfilled steel tonnage is, of course, the barometer of industrial conditions generally, but it is particularly the barometer of the ferro-alloy industry, because all metallurgical ferro-alloys are steel-making alloys and nothing else. The market in the past five years, with the exception of 1919, was largely a sellers' market, and competition is just beginning to be felt. Ocean-freight rates for both ores and alloys may be expected to be reduced, but production costs cannot show a downward trend until the present general inflation is over.

In normal times, Great Britain can dominate the American ferro-manganese market, but during the latter part of 1919, with exchange on London at $4.30, British labor costs lower than ours, and their fuel costs higher, domestic and British makers of ferro-manganese competed for the American market almost entirely on a delivery basis, because prices were practically the same. The trade situation in most metallurgical ores and alloys is one of the most important considerations before the domestic maker of ferro-alloys today, and many adjustments must be made to insure the future development of the industry of the United States.

SUMMARY.

The future of the ferro-alloy industry is bound up with so many conflicting factors and interests that it is unwise to indulge in considerations of too speculative a nature. Certain definite facts stand out very clearly, and we know the following: The electric furnace has made the growth of the industry possible, its prosperity is closely connected with the rise and fall in the steel trade, the further development and use of alloy steels is certain to continue and at the same time increase the normal demand for all kinds of ferro-alloys, and it is highly desirable that the United

States continues to occupy an important position in the ferro-alloy industry of the world, not alone for the sake of supplying domestic steel requirements, largely or in part, or for the sake of additional government revenues, but also for the possibility that emergencies may again arise.

DISCUSSION.

COLIN G. FINK[1]: The paper that has just been presented by Mr. Anderson would lead one to believe the ferro-alloy industry in this country was in danger. There is quite a little tariff agitation, etc. Now I am very much interested to hear as to whom we should fear? Can England compete with our ferro-alloy industry or can Germany do so? I am just putting this as a question. I think the impression left by Mr. Anderson's paper is that if something is not done by the government so far as the tariff is concerned, or we do not improve upon the process, etc., that our ferro-alloy industry which prospered during the years of the war, is apt to decline again. I think there are a number of ferro-alloy people present here who feel somewhat differently about this matter.

DUDLEY HARDE[2]: It is not competition by Europe, it is Canadian competition that gives the manufacturers the most concern. Canadian makers can produce ferro-silicon cheaper than it can be produced in this country, and they are doing so today.

J. W. RICHARDS[3]: That is not only true of Canada but of Norway and Sweden. Some of the ferro-alloy plants in Norway and Sweden have shut down because of the inordinate demands of their laborers for high wages, but others are shut down principally because they can not compete with Canada.

While I am an enthusiastic advocate of the electric furnace wherever it can be used, I think we ought to recognize the fact that possibly the blast furnace may again come into competition with the electric furnace for the manufacture of some of these high percentage alloys. Enrichment of the air blast used, up to

[1] Head of Laboratories, Chile Exploration Co., New York City.
[2] Maine Power Sales Co.
[3] Prof. of Metallurgy, Lehigh University.

35 and 40 percent oxygen, is a possibility of the near future, and by that I mean the enrichment at such a low cost that it can be used in blast furnaces. Under those conditions, the blast furnace, now limited to 15 percent ferro-silicon, can possibly manufacture 35 or even 50 percent ferro-silicon. If it is a possibility to manufacture the latter in the blast furnace, the electric furnace will not be able to compete with it in the manufacture of standard ferro-silicon. I am speaking of the possibilities of the near future; I am convinced that we ought to take them into consideration.

COLIN G. FINK: Dr. Richards points out that we may be able to turn out 50 percent ferro-silicon in the blast furnace. I thought the electric furnace people had definitely shown that that was impractical, that one had to resort to the electric furnace for 50 percent ferro-silicon.

W. D. BANCROFT: I understand that Mr. Cottrell is very enthusiastic about the possibility of supplying either pure oxygen at a very low cost, or at any rate, air with a high oxygen content, and that he believes there is a tremendous future along that line.

J. W. RICHARDS: I do not know of any proof that 50 percent ferro-silicon cannot be made in the blast furnace. I believe that it is mostly a question of getting the temperature necessary for the reduction of more silicon; with the use of enriched air the required temperature can probably be obtained. If we want to make 15 or 18 percent ferro-silicon in the blast furnace, we have to use the highest blast temperature and a large proportion of coke; it does not strike me as being metallurgically impossible that with enriched air we may go up to 25 or 30 percent ferro-silicon, and possibly even up to 50 percent. I do not think it has been proved that it cannot.

E. O. BENJAMIN[4]: It might be well to remember that at the present time, where power is cheapest, in the Niagara section of Canada, that the cheapest oxygen that can be produced costs about 3 mills per cubic foot at the point of manufacture, and that it is commercially sold at not less than nine-tenths of a cent per cubic foot. The way laboratories and small consumers purchase

[4] Chief Chemist and Engineer, International Oxygen Co., Newark, N. J.

it they pay about 2½ cents; that may have something to do with the efficiency of production.

J. W. RICHARDS: I was not speaking at all of the present figures for producing oxygen; I was speaking of oxygen in enriched air at possibly $1.00 a ton for the surplus oxygen above normal.

COLIN G. FINK: Just to close this argument, (laughter), Dr. Richards, I am afraid, overlooks one advantage of the electric furnace, and that is the concentration of energy. You cannot concentrate the energy to the same extent in the blast furnace that you can in the electrical furnace. When it comes to making 50 percent ferro-silicon, you will have a hard job making it in the blast furnace.

J. G. DAILEY[5] (*Communicated*): With particular reference to the making of ferro-tungsten I think one not in intimate touch with its industrial manufacture would be fully justified in concluding, from reading the above papers, that no serious difficulties are experienced in the electric furnace reduction and production of ferro-tungsten; that "it is one of the easiest alloys to reduce"; that the metallurgical advances in its making have been practically negligible over the last few years, and finally that it is made by two-stage reduction with a current consumption of approximately 5 K.W.H. per pound of contained tungsten produced and a tungsten recovery of from 80 to 90 percent.

I question if the larger producers would be satisfied to operate under such conditions or, in fact, could afford to operate under them with tungsten, in the ore, at from $16.00 to $20.00 per unit of WO_3 as it was, with some variations, for three or more years preceding the signing of the armistice. I know that at the plant of the Tungsten Products Co. of Maryland, at Baltimore, using such ores as the market afforded, recoveries materially in excess of 90 percent were consistently obtained with one-stage smelting operations and a current consumption appreciably under 2 K.W.H. per pound of contained tungsten produced, and producing a readily merchantable grade of ferro-tungsten.

Along the line of ferro-tungsten manufacture may I be permitted to ask a few questions:

[5] New Brunswick, New Jersey.

1. What is the largest size "button" of ferro-tungsten that it has been found economically practicable to make?

2. What means of breaking up "buttons" of ferro-tungsten has been found best?

3. In the two-stage production of ferro-tungsten has it been found more difficult to break up the high-carbon "buttons" resulting from the first smelting operation than to break up the low-carbon "buttons" from the second smelting operation, and if so how are these high-carbon "buttons" normally handled to break them up?

ROBERT J. ANDERSON (*Communicated*): In replying to the communication of Mr. Dailey regarding ferro-tungsten, it may also be advisable to amplify the remarks of Mr. Harde regarding competition in the ferro-alloy industry. Dr. Fink has put the question: "Can Europe compete with our ferro-alloy industry, etc.?" I think that there is no question as to what Europe can do in this industry. With the exception of ferro-vanadium, European ferro-alloy makers have dominated this industry at all times, with the exception of the recent war period. What was done in 1919 and in the present year is well known.

Mr. Dailey's remarks regarding the production of ferro-tungsten are interesting, particularly as to current consumption and recovery of tungsten. I cannot advise as to the "best" methods of operation, as suggested in Mr. Dailey's three questions.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 10, 1920, President Bancroft in the Chair.

THE POSITION OF THE ELECTRIC FURNACE IN IRON AND STEEL METALLURGY.[1]

By Lewis B. Lindemuth.[2]

ABSTRACT.

A detailed comparison is made between the physical and chemical characteristics and phenomena of the four steel-making processes—Bessemer, open-hearth, crucible and electric furnace. Undue praise and claims for the electric furnace method and process is deprecated, but its advantages are set forth in detail, with the conclusion that it is "an addition to and not a replacement of all the former skill in steel manufacture, and when it becomes understood as such * * * the position of the electric furnace in the industry will be as it should be, namely, that it is metallurgically the best steel-making instrument, and in its proper place also the most economical." [J. W. R.]

The use of the electric furnace in the manufacture of iron and steel has made possible the application of processes which represent a real advance in the art. This is accomplished by the ability to obtain in the electric furnace conditions similar to those of any other process. The oxidizing features of the Bessemer process may be obtained and the benefits of this condition utilized, and in the same heat of steel the reducing conditions of the crucible process may be applied, thus securing the refinements of the crucible process.

In addition to the ability to secure the advantages of any combination of other processes, the electric furnace makes possible conditions which have not heretofore been realized, such as reducing conditions in a basic container and a control of temperature not possible in any other process.

[1] Manuscript received March 10, 1920.

[2] Consulting Metallurgist, New York City.

The position of the electric furnace is unique. The number of installations has increased rapidly in the past few years with, of course, an ever-increasing demand for operators. As the principles of all processes can be carried out in the electric furnace, it is necessary for the operator to understand these principles in order to secure the desired results. Thus a man familiar with the open-hearth processes and nothing more would probably be mystified at some of the results he would obtain and being accustomed to making the steel as hot as it is possible for the open-hearth to make it he will be very much surprised and perhaps disconcerted at the result of applying the same practice to the electric furnace. On the other hand, a crucible man will run into phenomena which he probably never knew existed.

Another condition which has placed the electric furnace in its present position is the competition in the manufacture and sale of electric furnaces. Electric furnace designers and builders are for the most part not very familiar with their operation, and from the results obtained by some users of electric furnaces have based claims on their product which do not materialize under other users unless the furnace is properly handled.

It is therefore unfortunate, but probably natural, that such an advance in the manufacture of steel should be accompanied by disappointments and in many cases apparent failure.

It is easy in the electric furnace to manufacture steel of a quality as poor as the worst product of any other process and the mere fact that steel comes from an electric furnace signifies nothing as to its quality. Superior steel is therefore not a natural product of the electric furnace, but the product of a process made possible by the electric furnace.

There are many plants operating electric furnaces properly and producing steel equal to, and in many cases superior to, crucible. There are also plants operating improperly and making a product which is inferior to the average open-hearth steel. It is easy to see how much a condition would lead to the discredit of the whole product of the electric furnace from the consumer's point of view.

On the other hand, some manufacturers of electric furnaces have made extravagant and even ridiculous claims for the product of electric furnaces, both as to quality and cost of production, which have probably induced some manufacturers not familiar

with the production of steel to install electric furnaces for economical reasons which never materialized. This in turn would tend to discredit the electric furnace among manufacturers.

For example, in a paper presented before one of the prominent engineering societies this winter, figures for production costs and physical properties were given which were far from representing existing conditions.

In the first place there was a comparison between the physical properties of open-hearth and electric-furnace steel, heat treated. These properties were as follows:

	Open-Hearth	Electric-Furnace
Elastic Limit (lb/sq. in.)	41,060	64,850
Tensile Strength (lb./sq. in.)	89,100	105,140
Elongation (percent in 2 in.)	21.5	22.0
Reduction of Area (percent)	31.74	52.37
Fracture	Granular	Silky Cup

Both steels are described as receiving the same heat treatment. The paper evidently intends to convey the impression that each of these tests is characteristic of the product of the process by which it was made. A single glance at the results of the heat-treated open-hearth steel indicates that there is something very wrong. Either there was a mistake in recording the temperatures obtained or the heat treatment designed was not the proper treatment for the steel, or both. I have heat-treated a similar product of about the same section of open-hearth steel, and obtained consistently the following properties:

Elastic Limit (lb./sq. in.)..... 90,000
Tensile Strength (lb./sq. in.)....120,000
Elongation (percent in 2 in.).... 20.0
Reduction of Area (percent).... 61.0
Fracture.....Silky cups, half cups and mitres

I do not mean to say by this that open-hearth steel is superior to electric-furnace steel, but I do want to emphasize the fallacy of attempting to draw any conclusions from such figures. There are many kinds of open-hearth steel and electric steel, and such a "blanket" comparison as that just given indicates nothing for or against anything.

At another point in the same paper the cost of producing steel was given at a figure lower than the cost of operating a furnace, exclusive of the cost of scrap, and lower than the market price of heavy melting steel scrap at that time. If these costs were true it would mean that it would be profitable to use the electric furnace for the production of heavy melting scrap for use in an open-hearth charge. Needless to say, no one is doing this.

Another idea of electric furnaces is that electricity has an effect on the properties of the steel or acts as an aid to some mysterious additional refining. Such, however, is not the case. Its effect is only that of producing temperature, and in arc furnaces, which are practically the only ones in commercial use, a circulation of the bath, if there were any, due to electricity would be negligible compared to ebullitions which take place during the natural refining of the metal, and would not contribute to the quality of the steel produced.

The superiority of electric steel depends simply upon the application of principles not possible in either the crucible process nor the open-hearth process. To understand the reason for the electric furnace's superior product, the basic principles of steel manufacture and their application must be understood.

Principles of Oxidation and Reduction.

One of the two fundamental chemical principles in manufacturing steel is oxidation and reduction, which consists of taking oxygen away from certain of the elements encountered in steel making by adding other elements with which the oxygen will combine. For example, we add silicon to steel which we think contains iron oxide in order that we may obtain iron and silicon oxide. This represents oxidation of silicon and reduction of iron oxide.

The second chemical principle employed is that of combining bases and acids so that they will flux and form a slag. Oxides of basic elements will combine with oxides of acid elements but acids will not combine with acids and neither will bases combine with bases. As the oxides of the basic and acid elements are necessary for the application of the principles of bases and acids, oxidation and reduction might be considered the prime principles in iron and steel metallurgy.

A brief review of the iron and steel processes will demonstrate the importance of the principles of oxidation and reduction, and will show the flexibility of the electric furnace in meeting the predominating features of every commercial process.

Blast Furnace.

In the blast furnace iron ore, which is iron oxide, is mixed with coke and limestone and a blast of air blown into burning coke to produce the necessary heat for the reactions. There is an excess of coke over that required to produce the heat so that there is an incomplete oxidation of the coke. The gases resulting from this incomplete oxidation combine with the oxygen of the ore, and of the impurities of the ore and coke, and form metallic iron, manganese, silicon and phosphorus. The limestone after being calcined in the blast furnace combines with the oxide of silicon in the ore and coke and removes this impurity as a slag. Coke and ore both contain oxide of phosphorus, which is an acid, and were it not for the reduction of the phosphorus combined with the coke and ore, the phosphorus oxide would join the basic lime and pass off with the slag. As it happens under these reducing conditions the phosphorus, which is an undesirable impurity, all enters the pig iron. The blast furnace process is therefore entirely reducing and only pig iron is expected from a blast furnace. The metallurgical principles of the blast furnace may be approximated in an electric furnace.

Bessemer Process.

The Bessemer process is of two kinds—acid and basic. In both of these the principles of the blast furnace are reversed. Air is blown through molten pig iron, carbon, silicon, manganese and some iron are oxidized, and, in the case of the basic converter, phosphorus. In the acid process silica is the acid, iron and manganese the bases. These join together to form the slag. The oxide of silicon is the predominating element in this slag, and it is therefore acid in character. Phosphorus, which is a weaker acid than silica, will not join with the iron and manganese, and if oxidized at all will return to the steel. Sulphur, which is also a weak acid either oxidized or unoxidized, acts the same as phosphorus, and there is therefore no elimination of phosphorus or

sulphur in the acid converter. The fact that sulphur and phosphorus and iron oxide are injurious elements in steel limits the product of the Bessemer process both as to quality and as to the nature of raw materials which may be used.

The basic Bessemer uses a converter lined with basic materials and requires an iron very low in silicon in order not to destroy the basic lining and very high in phosphorus in order to produce the necessary heat. Air in the basic process oxidizes phosphorus, silicon, manganese, carbon, and some sulphur. The phosphorus in this case after being oxidized is brought into contact with a strong base by the addition of lime. The same applies to sulphur, and in the basic process therefore phosphorus and sulphur are removed. The iron oxide impurity is still present as in the acid Bessemer. The basic Bessemer process is therefore limited in quality of product and in the nature of the pig iron which can be employed. This process is not in use in the United States. The Bessemer process, both basic and acid, is therefore an oxidizing process and has its limitations as to quality of product. These oxidizing principles may be secured in an electric furnace.

Open-Hearth Process.

The open-hearth process is also of two kinds, acid and basic. The principles for the removal of impurities in the open-hearth are the same as those in the Bessemer with regard to phosphorus and sulphur. The open-hearth furnace's charge consists of approximately one-half pig iron and one-half scrap, and the fuel, instead of being elements contained in the charge, as in the Bessemer, is gas, oil or powdered coal, using preheated air for combustion. In order to obtain the maximum temperature in an open-hearth furnace or in any furnace using a flame for its heat, complete oxidation of the fuel must take place. Complete oxidation in turn requires an excess of oxygen over the theoretical amount. The charge in the open-hearth furnace is therefore subjected to oxidation at all times during the melting of the charge, although the intensity of the oxidation is not nearly as great as that of the Bessemer.

There are various modifications of the open-hearth process, devised for the handling of raw materials of various composi-

tions. They are all, however, oxidizing, and the process is therefore limited as to quality.

Open-hearth furnaces are most economically operated in comparatively large sizes, and the quality is again limited on this account in a manner which I will explain later.

All conditions of the open-hearth may be secured in an electric furnace.

Crucible Process.

The crucible process is simply a melting down operation. Small charges of about 80 to 100 lb. (40 to 50 kg.) are placed in clay crucibles or crucibles made from a mixture of clay and graphite. These are placed in a regenerative furnace and the charge is melted without coming in contact with the flame. The atmosphere in a crucible during melting is not oxidizing, and in the case of crucibles made from a graphite and clay mixture is reducing. Crucible steel is therefore practically free from the impurity iron oxide. Crucibles being acid, sulphur and phosphorus are not removed, and being reducing, manganese, which if oxidized would combine with the acid walls of the crucible, is not oxidized and remains in the finished steel in the same percentage that was in the charge. This necessitates high-grade materials for the charge, for only the highest grade steels can be manufactured by the crucible process on account of the expense involved. The product of the crucible is poured into ingots of as small a size as can be used. The crucible process is therefore limited to the conversion of already highly refined iron or steel, and at a cost several times greater than that of the open-hearth process.

Electric Furnace Process.

The electric furnace process is also of two kinds, basic and acid. The fuel in this process does not depend upon elements in the charge nor upon a flame development. It is simply the heat of the electric arc which is neither oxidizing nor reducing. This means that it is possible in an electric furnace to produce either a condition of oxidation or reduction, as desired, and in any sequence necessary. Therefore the oxidizing conditions of the Bessemer process for the elimination of silicon, manganese, carbon, and phosphorus may be obtained and the reducing conditions

of the crucible secured, with the additional advantage over the crucible that in the b a s i c process sulphur may be removed with ease to the minimum, which is not possible by any other process.

Any grade of steel or iron scrap may be employed for the production of the highest grade finished steel.

To accomplish a complete refining the basic process is necessary, and it must be conducted in two stages. In the first stage, oxidizing conditions are produced by the addition of oxygen in the form of iron ore. In this period phosphorus and manganese are removed and a portion of the carbon, if desired. The slag containing the phosphorus is removed from the furnace and materials for second slag containing a high percentage of lime are added. On top of this slag is thrown ground coke or coal, which produces the necessary reducing conditions. These reducing conditions are so strong that a calcium carbide slag is formed and silicon, vanadium, or other easily oxidized acid elements may be added to the steel in the presence of basic slag and lining without the loss of even a small percentage of them. All iron, manganese, phosphorus, chromium or other metallic oxides and even, at times, silicon will be reduced from this second slag and pass back to the metal. The basic electric furnace process therefore makes it possible to apply all of the principles employed in the refining by the Bessemer, open-hearth and crucible processes in making any one heat of steel.

The acid electric furnace process, which has been advocated considerably of late, does not allow the complete application of all these principles and it is very questionable if, under the most skillful supervision, acid electric furnace steel can be made of a quality equal to that produced by the basic process.

In the basic process the steel is covered by a slag entirely devoid of oxides except lime, magnesia, silica, and perhaps alumina. None of these oxides, however, is oxidizing to the steel. In the acid electric process, however, the slag, even under the most skillful supervision, contains a certain percentage of oxides of iron and manganese in addition to oxides of calcium, silicon and aluminum. The acid slag is a complex calcium-iron-aluminum silicate, which is itself oxidizing.

In a paper which I gave before the American Foundrymen's Association at its last meeting in Philadelphia, I explained why

it was impractical to obtain reducing conditions in the acid electric process similar to those in the basic. I will summarize this briefly:

In melting down a charge in an acid-lined furnace the slag is made up principally of iron and manganese silicates, the percentage depending upon the amount of manganese in the charge and the condition of the scrap with respect to rust. The usual slag immediately after melting shows about 50 to 55 percent SiO_2 and 45 to 50 percent FeO and MgO. Immediately after this slag is formed it will tend to adjust itself to a certain degree of basicity and this degree is practically constant regardless of whether the bases are iron oxide, manganese oxide, lime or magnesia. In comparing slags for their relative basicity the percentage of bases does not represent this. For example, if we assume that one unit (molecule) of FeO combines with one unit (molecule) of SiO_2 the percentage of FeO would be 54.5. Also if one molecule of CaO combines with one molecule of SiO_2 the percentage of CaO would be 48.2, although the latter slag would be as basic as the iron silicate slag containing 54.5 percent FeO. It is therefore necessary for comparative purposes to reduce all of the bases in the slags to be compared to the equivalent of one of these bases. This equivalent is proportioned to the molecular weight of the oxide of the base. As FeO is the common element we may base our comparisons upon it and it follows that one (molecular) unit of CaO is equivalent to 1.28 (molecular) units of FeO and that one (molecular) unit of MgO is equivalent to 1.9 (molecular) units of FeO. The molecular weights of MnO and FeO are so nearly the same that for all practical purposes they may be considered as equal. If we then look at acid slags from the viewpoint of their degree of basicity, we find that we cannot reduce FeO from an acid slag by the production of reducing conditions. In other words, in the acid process iron oxide must be replaced by a stronger base, and to secure the best results this base must be one which will combine with silica in such a manner as to produce a silicate which is not oxidizing. The best available base for this purpose is lime. Manganese can be used, but manganese silicate is oxidizing. However, I believe that as we cannot readily obtain reducing conditions, we are better off adding both manganese and lime to secure what beneficial results manganese may

have upon the steel. The two following analyses are an example of the degree of basicity being practically the same in slags which are apparently entirely different by analysis:

Element	Slag No. 1 Percent	Slag No. 2 Percent
SiO_2	53.46	56.60
CaO	7.60	20.00
MnO	20.22	9.08
FeO	11.38	4.44
MgO	4.86	4.80

Slag No. 1 figured on a basis of FeO equivalent represents 49.07 percent, while slag No. 2 on the same equivalent basis equals 49.09 percent. The iron oxide in slag No. 2 is as low as it is probably possible to obtain it in the electric furnace excepting under the most favorable conditions, but no actual reduction of oxides has taken place in the slag.

If, when melting down, the slag is high in bases these bases will combine with the silica lining of the furnace and adjust themselves to a fixed degree. On the other hand, if the melting down slag is high in silica due to hearth bottom material or sand in the scrap, and there are no bases available with which it can combine, silica will be reduced to silicon and will pass into the metal, thus relieving the slag of some of its excess acid. This reduction of silica does not necessarily mean deoxidized steel because of the variation in affinities between oxygen and silica at high temperatures. The following two slags taken from the same heat to which no additions have been made illustrate how a slag high in bases will adjust itself:

Element	Slag No. 1 Percent	Slag No. 2 Percent
SiO_2	39.12	55.10
CaO	6.55	5.27
MnO	25.35	23.63
FeO	23.77	11.30
MgO	0.22	0.23

The iron oxide equivalent of bases in slag No. 1 is 57.77 percent, and in slag No. 2, 41.98 percent. As an example of a slag

high in acids, which tended to adjust itself, seven slag and metal tests were taken throughout a heat in which the original iron oxide equivalent of bases amounted to 38 percent. This equivalent increased to 42.6 percent, and the residual silicon in the steel increased from 0.11 to 0.32 percent without additions of silicon. It is not, therefore, possible in the acid electric furnace process to reach the degree of refinement which can be obtained in the basic process. The product of the acid electric furnace, as it is commonly conducted, represents the quality which is usually produced by the acid open-hearth process, and the fact that it comes from the electric furnace does not add to its quality. The statement that acid electric furnace steel is a cleaner steel for castings has not to my knowledge been demonstrated, and I firmly believe that if foundries experiencing trouble from dirt in their castings in using the basic process investigate carefully their ladle practice, lining materials, skimming device, etc., and also analyze some of the dirt which they find in their steel, they will discover that there is no connection between dirty steel and the basic process.

As for the acid process being faster than the basic process, this is also a misrepresentation. The acid process, as commonly conducted, is a one-slag operation and the steel produced is of open-hearth quality. If open-hearth quality steel is what is desired and steel such as is usually made in the acid electric furnace, the same speed can be obtained in the basic furnace by making steel of basic open-hearth quality.

In many cases steel of open-hearth quality is all that is required from electric furnaces, but in such cases the purchaser of the steel should be acquainted with the fact and his price adjusted accordingly, otherwise the misrepresentation of facts cannot help but react upon the electric furnace process.

PHYSICAL METALLURGY.

The physical metallurgy of steel manufacture is entirely separate and distinct from its chemical metallurgy and it is in this that the greater danger of producing very inferior steel by the electric furnace process is encountered, on account of the possibility of obtaining higher temperature than in any other process.

Solidification of Molten Steel.

Solidification of molten steel embraces many phenomena which have a great influence upon the properties of the finished product. As an example, we will take steel cast into an iron mold of square section. The mold, no matter to what temperature it is heated, is cold in comparison with the steel which is poured into it. The first metal to solidify is that which comes into immediate contact with the mold. In the case of many alloy steels and at times in carbon steels this quick solidification next to the walls of the mold forms a structure which has a needle-like appearance known as columnar crystallization. These columnar crystals are perpendicular to the walls of the mold, their depth depending upon the grade of steel and the relative temperatures of the steel and mold. The appearance of these crystals around the edge of an ingot broken transversely is much like a miniature of the Palisades of the Hudson. After the formation of the columnar crystals, solidification is a growth of crystals of the pure steel perpendicular to the sides of the ingot and extending in, which have the appearance of fir trees and are commonly known as fir-tree crystals. These crystals have branches which in turn branch and would look (if the ingot were bled) like a small forest growth along the solidified wall of the ingot. Impurities in the steel, including sulphides, silicates and non-metallic impurities, are pushed forward by these growing crystals so that the remaining molten steel is constantly being enriched with impurities. Therefore, the last metal to solidify contains a higher percentage of carbon, manganese, phosphorus, sulphur and non-metallic impurities than the portion of the ingot which solidified first. This collection of constituents of the steel and impurities in the last part of the ingot to solidify is known as "segregation." At the same time that the steel is solidifying it is cooling off and therefore shrinking in volume from the center toward the outside. The effect of this shrinkage of course will be in the last portion of the ingot to solidify, which is the top and central part. A shrinkage cavity is formed which extends down the central part of the ingot sometimes as much as 60 percent from the top, and causes the defect designated as a "pipe."

Another phenomenon of solidification which causes defects in ingots is the formation of blow holes. Steel, if not properly made,

will contain gases, excess oxides, and the latter, if metallic, will combine with carbon in the steel forming a gas which makes cavities in the ingot. Rusty molds will cause blow holes on the surface of the ingot by a reaction between oxygen of the rust and carbon in the steel, forming a gas. Moisture is still another source of blow holes, as moisture is immediately converted into superheated steam, which, if it has no place to escape, will be trapped in the steel.

From this brief outline of solidification it can be seen that temperature of casting and rate of cooling of masses of steel are factors as great as, if not greater than, any possible variations in furnace practice. A heat which is too hot will produce larger columnar crystals. It will cool more slowly and give more time for the segregation, and with slower cooling there is a larger crystallization which is sometimes sufficiently marked to persist throughout all subsequent mechanical and heat treatments. Furthermore, the higher the temperature at which the steel is cast the greater will be its shrinkage and hence the larger percentage which will be affected by pipe.

Referring again to the chilled section immediately adjoining the mold, called "columnar crystals," these crystals being perpendicular to the walls of the mold will meet at the corners of the ingot in a line representing the diagonals of the mold, and at the bottom of the ingot where the chilling effect of the bottom and the sides combine, the planes of the junction of the columnar crystals represent a distinct pyramid or frustrum. The junction of these crystals has no strength and often is seen in the ingot as openings into which a knife blade can easily enter. A steel ingot with this defect would have no strength transversely on the corners. It would probably roll or forge poorly and often result in a failure of the steel in service which could not be explained from analysis, heat record, microscope, or the fact that the steel was made in the Bessemer, open-hearth, crucible, or electric furnace. The only remedy for this defect is the proper design of molds, and control of pouring temperatures.

Non-Metallic Inclusions.

Non-metallic inclusions, usually designated by consumers of steel by the indefinite terms of "slag" and "dirt," are supposedly

of two origins. First, the formation of non-metallic compounds are supposed to result from reactions of the elements in the steel during the steel-making process; many of these supposedly do not float out of the steel either in the furnace or during solidification in the molds. It is assumed that iron oxide in the steel will combine with silica to form an iron silicate. Similarly, manganese silicates are formed, manganese sulphides, and if aluminum is added, aluminum oxides or aluminum silicates. All of these compounds are of the nature of a slag and have less specific gravity than steel. The other source of foreign inclusions is from fusion of ladle linings, sand used around the nozzle of the ladle, fusion of nozzles, stoppers and sleeves and dirty asbestos or clay which is sometimes used to seal the bottom of the molds. Evidence of inclusions from nearly all of these causes can be found in many steel plants, the frequency of their occurrence depending upon the care exercised in preventing them. What proportion of these non-metallic impurities comes from reactions within the metal and what proportion from foreign materials outside of the elements in the steel is difficult to estimate. It has been my experience that the greater proportion comes from sources outside of the furnace. It would therefore follow that no matter what process is used in making the steel, if the details of handling after it leaves the furnace are not taken care of most scrupulously, foreign inclusions will result, and it further follows that the higher the temperature of the steel leaving the furnace the greater will be the possibility of such inclusions. A large percentage of such inclusions, even though of considerably less specific gravity than the steel itself, cannot float to the surface on account of the net work of "fir tree crystals" through which it must pass, and, also, very fine inclusions will remain in the steel in the same manner in which dust of higher specific gravity than the air will remain suspended in the air for a considerable period.

Torn Ingots.

Still another very common defect in ingots which occurs regardless of the process by which the steel is made, is that of torn ingots. It must be appreciated that an ingot in solidifying shrinks longitudinally. Therefore, if for any reason such as rough molds, overfilling molds and causing a fin on top, or cracked hot-tops,

or hot-tops of improper design, the ingot cannot freely contract, it will crack horizontally in one or more places. This is merely a question of proper design of molds, and their rigid inspection, proper selection of hot-tops, and the careful setting up of the molds. It is not dependent upon any quality of steel leaving the furnace.

Another common cause of ingot defects is poor pouring practice. If steel splashes on the side of the mold it will solidify immediately and stick. The surface of the splash becomes oxidized and as the mold is filled the splashed portion will be included in the ingot unquestionably and cause an internal defect.

I have just enumerated a lot of things which can happen to steel and there are still a number which I have not mentioned. Not one of these is any more related to the electric furnace process than it is to the Bessemer, open-hearth or crucible. The reason for mentioning them is simply this: It must be understood that all grades of steel are dependent upon many factors, outside of the process by which they are made, for their quality. If a man buys electric-furnace steel he has no assurance that he is buying a superior product simply because it is electric-furnace steel unless he purchases it from a manufacturer of repute by whom all of these things are recognized and provided for.

The manufacture of high-grade steel is simply a continuous sequence of one detail after another, and the process by which the steel is made is merely the starting point toward quality.

ECONOMICS OF THE ELECTRIC FURNACE PROCESS.

Many cost-sheets of the production of electric-furnace steel are published by manufacturers of electric furnaces. I have not yet seen one in print which was possible under the conditions existing at the time it was printed. The example I gave in the first part of the paper is typical. In considering the cost of operating the electric furnace, the quality of steel desired must be determined first. If steel of open-hearth quality only is sufficient, it can be manufactured more cheaply than steel of the highest quality.

Generally, an electric furnace used for melting cold material will require a charge of at least one-third fairly heavy steel scrap, the balance of light material. Forty pounds (18 kg.) of electrodes

will be consumed per ton of steel produced and about 850 K.W.H. of power required for two-slag heats. About eight men are necessary to handle a 6- to 10-ton furnace, with an average wage of about 150 percent of that of common labor. At today's prices, furnace repairs and relining average about $3.00 per ton, and materials for operating, including molds, fluxes, manganese and silicon additions, about $6.00 per ton. These figures represent the probable actual expenditure over a period of time sufficiently long to include repairs to the furnace, relining, and installing new bottoms. For small steel castings the electric furnace in most localities competes successfully in cost with the converter. Particularly at the present time when the differential between the price of pig iron (a large percentage of which is necessary for the converter) and steel scrap for the electric furnace is very great. In the manufacture of castings also it is possible to obtain a temperature in the electric furnace sufficiently high to produce castings which until recently were impossible. In competition with the open-hearth the electric furnace in small foundries has a decided advantage in view of the fact that the usually larger-sized heats of the open-hearth cannot be completely poured before the steel has cooled to a point which gives a high percentage of defective castings.

In districts remote from the general steel centers the electric furnace, with reasonable power rates and with a decided advantage in freight rates, can compete successfully with the open-hearth in the production of all grades of commercial steels. The electric furnace may also be profitably used for the manufacture of pig iron from steel scrap where costs of raw materials and power make it economical.

The tendency in electric furnaces is to use those of larger capacities, which have now reached forty tons, in conjunction with a converter or open-hearth. In these processes the electric furnace is not used for melting scrap but merely adds the final reducing and desulphurizing slag to steel already refined by one or more of the other processes. The real advantage of the electric furnace lies in its ability to produce reducing conditions as the final stage. Where melting costs and preliminary refining costs are higher with the electric furnace than with other processes, the

only economy in a plant equipped with other processes is to use it only for this final refining, in the production of the highest quality steels.

CONCLUSIONS.

The electric furnace from the metallurgical point of view permits more flexibility in the application of processes and varieties of product than any other steel-making furnace yet devised. Its flexibility requires more knowledge on the part of the operator as to principles, because of the fact that he can apply any one of them, whereas all other processes require knowledge of only the limited principles involved in that particular process.

Electric-furnace steel can and should be superior to other grades of steel, but it is so only when properly made and when the phases of manufacturing steel other than the melting have been properly provided for.

Too little knowledge on the part of the operator and, we might say, over enthusiasm on the part of salesmen in introducing furnaces where the economics do not permit, have jeopardized the position of the electric furnace and have made both the product and the economy often questionable.

The electric furnace is an addition to and not a replacement of all the former skill in steel manufacture, and when it becomes understood as such and when the sale of one furnace which brings returns to its owners is realized to be a better advertisement than the sale of two furnaces only one of which is successful, the position of the electric furnace in the industry will be as it should be, namely, that it is metallurgically the best steel-making instrument, and in its proper place also the most economical.

DISCUSSION

F. W. BROOKE[1]: If I may be allowed to at least defend, in a small way, the manufacturers of electric furnaces, I would like to refer to one sentence in this paper. It says that electric furnace designers and builders are not, for the most part, familiar with

[1] Vice-President, The Electric Furnace Construction Co., Media, Pa.

their operations. Now I really do not think, Mr. Lindemuth, that that is a fair statement, if you look upon the leading furnaces today, and, in a rough way, I might just mention three leading furnaces, the Heroult furnace, the Rennerfeldt furnace and the Greaves-Etchells furnace. I think that everybody will concede that Mr. Heroult knew probably more about operating furnaces than any other man living up to the date of his death. And I might say also that Mr. Heroult was a great competitor of our own company. I do not know whether Mr. De Freis, who is connected with the Rennerfeldt furnace, is here or not, but he certainly does understand the operation of copper and other furnaces. In the case of our own company, every member of our technical department has not only run a few heats but has had years of experience; I know that in the case of myself and our President, we were in this field ten years ago when electric furnaces were hardly understood, and I just make that statement as a defense for electric furnace manufacturers.

J. W. RICHARDS[2]: I think that the author, although he has made some very complimentary references to the electric furnace and its possibilities, has been even too modest in showing what it may become. The treatment of the melted charge in the electric furnace is a different field, perhaps, from the treatment of cold charges. Cold charges are used for specific purposes, for making fine quality steels, but the treatment of melted pig iron or melted steel from other furnaces is a field which is going to increase and become, I think, the predominating use of the electric furnace in the steel industry. We have now the Duplex and Triplex processes, by which steel is made in the cheapest way possible first by the Bessemer or open hearth, or the combined Bessemer and open hearth, and then, when finished as far as those processes are concerned, it is put into the electric furnace to receive the finishing touches which these other furnaces cannot give it. You cannot keep steel melted in an open-hearth furnace without continuously oxidizing it, since it is subjected to oxidizing conditions all the time from the products of combustion; in the electric furnace it can be kept melted under reducing conditions and given

[2] Professor of Metallurgy, Lehigh University, Bethlehem, Pa.

a dead melt which is the exact duplicate of a dead melt in a crucible. Therefore the first use of the electric furnace is to give the finishing touches to steel which is otherwise unfinished in the cheaper Bessemer and open-hearth furnaces. That, in my opinion, is going to be the largest use of the electric steel furnace; in fact, I think the cost of doing this is so small that it means the addition on an average of only one dollar per ton for keeping the metal melted half an hour to an hour and a half in the electric furnace. That small additional cost, which means giving it just the finishing touches, is practical and this, when realized, will lead to one of the largest uses of the furnace. Prof. Eichoff, with whom I exchanged this opinion, said to me, "I believe that all steel will sooner or later be put into the electric furnace to give it its finishing touches, because the cost of doing so can be, by proper organization of the steel furnaces, reduced to such a small amount that it will pay to do it." I think that the time is coming in a few years when the electric furnace will be a part of the equipment of every steel works and the ordinary grade of steel is going to be improved many percent by this very cheap treatment.

L. B. LINDEMUTH (*Communicated*): Referring to Mr. Brooke's statement, I will say that the sentence which he quotes was probably not well worded. What I really should have said was, that electric furnace designers and builders are not, for the most part, familiar with the manufacture of steel. The manufacture of steel goes much further than the furnace or process in or by which it was made. There are of course exceptions to my statement, but our opinion of the knowledge, ability and integrity of the manufacturer of an electric furnace must be judged by the literature and publicity regarding these furnaces, and as we do not care to find another motive for the literature we must blame it upon unfamiliarity with the subject treated.

Professor Richards is perfectly correct in his statement regarding the economy of an electric furnace when used as a final treatment for melted steel. In some parts of Europe, where steel is now made by the basic Bessemer process, the conclusion that an electric furnace will be the final treatment for a large part of steel is probably justified.

As a supplement to the open-hearth process this is very problematical. One of the greatest influences upon the quality of steel is the size of the ingot. If electric furnace steel is to be cast in the same moulds as open-hearth steel for the production of such articles as are now made from open-hearth steel, it is possible that the large size of ingot will make it impossible to find in the product an increase in quality which will warrant the cost of additional refining by the electric furnace.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

THE MANUFACTURE OF HIGH SPEED STEEL IN THE ELECTRIC FURNACE.[1]

By Roy C. McKenna.[2]

Abstract.

A detailed description, from the manufacturer's standpoint, of the advantages of the electric furnace process over any other way of making high-speed tool steel. The details of charging, melting, slagging, teeming, forging, heat-treatment, etc., are all discussed, and the various important points in the electric furnace practice given. [J. W. R.]

High-speed steel is a tool steel that possesses the property known as red-hardness; that is, the property of maintaining its hardness or cutting edge at relatively high temperature. This property is imparted to tool steel to the greatest degree by the introduction of tungsten and chromium. Commercially, high-speed steel may be considered as a tool steel containing between 16 and 20 percent tungsten, and from 3 to 5 percent chromium. All of the recognized high-quality brands of high-speed steel contain vanadium, generally about one percent.

The invention of high-speed steel is accredited to Messrs. Taylor and White, and was developed at the Bethlehem Steel Co. plant about the year 1898, being demonstrated commercially first at the Paris Exposition in 1900. In the early days all high-speed steel was melted by the crucible process. For centuries the highest quality tool steel had been melted by the crucible process. The electric furnace had many theoretical advantages over the melting of tool steel by crucible process, but it is with reluctance that

[1] Manuscript received March 8, 1920.

[2] President, Vanadium-Alloys Steel Co., Latrobe, Pa.

manufacturers of tool steel recognize that the advantages of electric furnace melting over crucible melting are real. Good tool steel has been made by the crucible process for years; the trade preferred tool steel manufactured by the crucible process, and the electric furnace had to win its way in the manufacture of tool steel, and had to thoroughly demonstrate to the manufacturer of tool steel its decided advantages over crucible melting, and to prove conclusively that a higher quality and more uniform tool steel could be furnished by electric furnace melting.

All makers of high-speed steel strive to produce a steel of uniform quality, which when heat-treated by customary practice, or by following special instructions issued by the maker, gives uniform and satisfactory service. No other element bears as important a relationship to proper heat-treating temperatures as carbon. For this reason uniformity of carbon content is of the utmost importance, and this uniformity can best be obtained by electric furnace melting.

The great benefit of having vanadium in high-speed steel is recognized by all and disputed by none. Thousands of actual tests thoroughly demonstrated the superiority of high-speed steels containing vanadium over those not containing this valuable element. It is true that there is a wide range of vanadium content in various recognized and reputable brands of high-speed steel. It is the consensus of authoritative opinion that high-speed steel containing approximately 18 percent tungsten and 4 percent chromium should contain one percent vanadium. Ferro-vanadium, on account of its relatively low specific gravity and relatively high melting point, is difficult to introduce into steel melted by the crucible process. A wide range of vanadium content in high-speed steel manufactured by the crucible process must be permitted. By the electric furnace process the vanadium content of high-speed steel can easily be maintained within much narrower limits; inasmuch as it is the aim of all makers to maintain individual uniformity of their product, this is an advantage, although not to the same degree as the control of carbon.

The great advantage of the electric furnace over the crucible is its capability of producing steel low in phosphorus and sulphur. Sulphur in steel causes "red-shortness" or brittleness when hot. Sulphur promotes the segregation of impurities, forms sulphides,

causing slag pockets and blow-holes, impairing the density and homogeneity of steel. It is never uniformly distributed throughout the steel, and is therefore responsible for weak spots and defective areas.

Phosphorus causes "cold-shortness"; it also promotes the segregation of impurities. It causes brittleness and increases breakage losses. Phosphorus is never uniformly distributed throughout steel and impairs the homogeneity and soundness of the metal. It is the worst enemy of tool steel. Reliable analyses of 300 consecutive heats of high-speed steel made in the electric furnace showed the following sulphur and phosphorus contents in percentages:

Heats		Sulphur		Heats		Phosphorus	
213	—	under	0.005	162	—	under	0.014
70	—	"	0.014	114	—	"	0.020
15	—	"	0.024	24	—	"	0.028
2	—	"	0.030				

To make tool steel or high-speed steel by the electric furnace process the equal of or superior to similar steel manufactured by the crucible process, it is necessary to give the same attention to the selection of base material and ferro-alloys entering into the mix as when melted by the crucible process. A low-phosphorus melting bar is essential as a base. Although it is true that the two enemies of tool steel, sulphur and phosphorus, can be partly eliminated by the electric furnace process, yet manufacturers of tool steel have learned from experience that to produce a "quality" steel it is necessary to introduce only the purest base and ferro-alloys obtainable.

The advantage of the electric furnace melting over crucible melting is that it enables the manufacturer to keep the contents of all elements entering into his product within much narrower limits than is possible by any other process, and to produce a steel of greater uniformity as far as chemical analysis is concerned.

It is difficult to set forth the advantages of electric furnace production of tool steels over crucible melting without apparently over-emphasizing the importance of chemical composition. Every advantage of electric furnace melting over crucible melting lies in the better control of the chemical composition of the product.

The chemical composition of tool steel for any purpose is a basic consideration and must be such as to answer requirements, but the quality of tool steel will always depend upon local conditions surrounding its manufacture. In order that good tool steel may be furnished in finished bars it must be of correct chemical analysis, properly melted and cast into solid ingots, free from blow-holes and surface defects. Sudden changes of temperature in high-speed steel are to be guarded against at every stage of its manufacture and subsequent treatment. Ingots of high-speed steel are relatively weak, and the tendency to crack due to cooling strains is great. For this reason the hot ingots are not allowed to cool quickly, but are placed in furnaces which are of about the same temperature and are allowed to cool gradually before being placed in stock. Good high-speed steel can be made *only* from good ingots.

The quality of high-speed steel is dependent to a great extent upon its structure. Please understand that by further reference to "structure" of high-speed steel is meant the appearance of a polished and etched specimen under the microscope. By "fracture" will be meant the appearance of the broken surface of a bar or billet to the naked eye. The making of the structure begins under the hammer, and the beneficial effects produced in this stage persist through the subsequent operations, provided they are properly carried out. The massive carbides and tungstides present in the ingot are broken down and uniformly distributed throughout the billet.

To accomplish this the reduction in area must be sufficient and the hammer blows should be heavy, so as to cause compression into the center of the billet; otherwise undesirable characteristics such as coarse structure and carbide envelopes will exist and cause the steel treater much trouble. Surface defects invisible in the ingot may be opened up under the hammering operation, in which event they are clipped from the hot billet.

Generally speaking, it may be said that high-speed steel of good quality works well under the hammer. Ingots are first hammered into billets. These billets are carefully inspected and all surface defects ground away or chipped. The hammered billets are again slowly heated and receive a second hammering, known as

"cogging." The billet resulting therefrom is known as a "cogged" billet, and is of the proper size for the rolling mill or for the finishing hammer.

Although it is not considered good mill practice, some manufacturers who have large rolling mills perform the very important cogging operation in the rolling mill instead of under the hammer. Cogging in a rolling mill does not break up and distribute the carbides and tungstides as efficiently as cogging under the hammer; another objection to cogging in the rolling mill is that there is no opportunity to clip surface defects developed as they can be under the trained eye of a hammerman, thereby eliminating such defects in the finished billet.

The rolling of high-speed steel is an art known to very few. The various factors governing the proper rolling of high-speed steel are so numerous that it is necessary for each individual rolling mill to work out a practice that gives the best results upon the particular analysis of high-speed steel they make. Important elements entering into the rolling of high-speed steel are the heating and finishing temperatures, draft, and speed of the mill. In all of these the element of time must be considered. There is no department of a tool steel plant where the personnel of the actual operators has a greater influence upon the quality of the finished product.

High-speed steel should be delivered from the rolling mill to the annealing department free from scale, as scale promotes the formation of a decarbonized surface. In preparation of bars of high-speed steel for annealing, the bars are packed in tubes with a mixture of charcoal, lime, and other material. The tube is sealed and placed in the annealing furnace. The temperature of the furnace is gradually raised to about 1650° F. (900° C.) and held there for a sufficient length of time, depending upon the size of the bars. After very slow cooling the bars are removed from the tube. They should then show a Brinell number of between 235 and 275.

The inspection department of a high-speed steel mill ranks with the chemical and metallurgical departments in safeguarding the quality of the manufacturer's product. They inspect all finished material from the standpoint of surface defects, hardness, size

and fracture. They reject such steel as is judged not to meet the manufacturer's standard. Various standards are set up by different manufacturers. Some standards are high, some low—according to the individual marketing policy of the manufacturer.

The inspection and metallurgical departments work hand in hand, and if any department is not functioning properly it will soon become evident to the inspectors, enabling the management to remedy the trouble.

The successful manufacture of high-speed steel can only be obtained by those companies who have become specialists. The art and skill necessary in the successful working of such steel can be attained only by a man of natural ability in his chosen trade, and trained under the supervision of experts. To become an expert operator in high-speed steel in any department of its manufacture, it is necessary that the operator work almost exclusively in the production of such steel.

The value of high-speed steel to the user depends upon its receiving proper heat treatment. It is not the writer's intention to take up the subject of heat treating. The purpose of heat treating high-speed steel is to produce a tool that will cut so as to give maximum productive efficiency. This cutting efficiency depends upon the thermal stability of the complex hardenites existing in the hardened and tempered high-speed steel. It is extremely difficult to convey the meaning of the word "hardenite" to those that do not have a clear conception of the term. The complex hardenites in high-speed steel may be described as that form of solid solution which gives to high-speed steel its cutting efficiency at high working temperature. The complex hardenites in high-speed steel are produced by heating the steel to a very high temperature, near the melting point, which throws into solution carbides and tungstides, provided that they have been properly broken up in the hammering process and uniformly distributed throughout the steel. By quenching the steel at correct temperature this solid solution is retained at atmospheric temperature.

As there are undoubtedly present many who have had much greater experience in the operating of electric furnaces than the writer, it has been my purpose only to set forth the particular advantages that the electric furnace possesses over crucible melting for tool steels, particularly high-speed steels. The writer has

assumed that his audience is informed as to the advantages of electric furnace melting over other methods of steel melting in higher quality tonnage steels and alloy steels.

You may, however, be interested to know that cost sheets show the average power consumption of a three-ton heat of high-speed steel melt in a three-ton Heroult electric furnace is 1000 kw. hrs. We use an average of 40 pounds (19 kg.) carbon electrodes per heat. The average life of a lining and roof for high-speed steel is about 80 heats, and our practice is to line the walls in a manner that will give us as many heats as we get from the roof, and to do this we use magnesite brick for a distance of about three feet (0.9 m.) in the wall back of the middle electrode. This part of the wall will then last as long as the balance of the lining, which consists of silica brick.

For the bottom of the furnace we use a double roasted, specially prepared dolomite, which is mixed with tar and pitch and rammed into place with a pneumatic sand rammer. A bottom put in in this manner will last from 400 to 600 heats.

It is the writer's opinion, as a manufacturer of tool steel, that by the use of the electric furnace a more uniform and homogeneous product is procured than is possible by any other method of melting.

DISCUSSION.

R. C. McKENNA: Mr. Norris stated that ferro-vanadium containing six to ten percent of silicon could be used in the electric furnace in the manufacture of high-speed steel. It has been used; but the only reason is because we had to use it to get the vanadium.

G. L. NORRIS[1]: I would like to correct the statement that Mr. McKenna attributes to me. I did not name the percentages of silicon, but I will say now that 20 percent silicon content in the ferro-vanadium has been successfully used and the silicon in the steel maintained below 0.25 percent.

F. W. BROOKE[2]: Mr. McKenna stated that one of the most important points in making high-speed steel was to add very pure

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[2] Vice-President, The Electric Furnace Constr. Co., Media, Pa.

alloys. That is partly so, but I think the steel maker also realizes another very important point, that is, not to add any of these alloys, especially ferro-vanadium, to anything but pure steel and pure slag; that is to say that the steel should be thoroughly deoxidized and the slag should also be thoroughly reduced before such an alloy as ferro-vanadium is added. One of the important properties of ferro-vanadium in the making of high-speed steel is its scavenging effect on the metal. If the slag is highly oxidized we are going to lose quite a percentage of this vanadium before it ever gets into the steel. That is probably an answer to one of the earlier papers which stated that the use of ferro-vanadium in steel in the earlier days was not very successful. I think that its success really dates back to manufacturing steel in the electric furnace. In the earlier days they had not got steel making down to such a fine science as today, and the making of an oxidized slag was not so thoroughly understood. It is also a matter concerning the analyst himself. To analyze for vanadium in the earlier days was rather a particular process, a flash method was used and the personal element entered into it very much, and the analyst, when he found this difficulty, was tempted to go around to the chart sheet and make his flash point coincide more or less with what he was supposed to get.

J. W. RICHARDS[3]: There is a point in the making of high-speed tool steel which is important in the electric furnace melting, and that is that when you make a high-speed steel with 20 or 25 per cent of tungsten, you are adding an extremely heavy metal and there is danger of the metal sticking on the bottom of the hearth and not becoming easily alloyed. In the crucible that would necessitate almost constant stirring or a great deal of stirring, in order to get a good alloy of the iron with the tungsten. In the electric furnace of a certain construction, the stirring is accomplished by the magnetic field which circulates the metal in a vertical direction, so that there are certain types of electric furnace which are most suitable for the making or melting of these alloys because of the stirring action which brings up the metal from the bottom and takes down the hot metal from the top. Also, those furnaces which have electrodes embedded in the hearth at the bottom of the furnace are more suitable for this material because the cur-

[3] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.

rent heats the bottom of the furnace as well as the surface of the metal, and thus facilitates the alloying of the metal, which tends to sink to the bottom.

C. A. WINDER[4]: In connection with that particular phase of the question, I would like to ask at this time whether Dr. Richards thinks that the induction furnace is a possibility in connection with the production of high-speed steel on account of the stirring action?

J. W. RICHARDS: The very rapid stirring action in the induction furnace is undoubtedly an advantage in that direction. On the other hand, if you are trying to refine steel, to take out silicon as suggested by Mr. Norris, and do any other refining, the induction furnace is not so well suited to that as other types of furnace.

F. W. BROOKE: I think it would perhaps be well to explain why the induction furnace is not quite suitable for that reason; the induction furnace must necessarily have a bath of "Doughnut" type, and that makes rather a bad roof construction and makes the manipulation of the slag extremely difficult.

FRANK HODSON[5]: Dr. Richards made a very good point on the importance of circulation in the bath when melting high-speed steel and suggests that this was due to magnetic effect. I should like to point out that in the Greaves-Etchells type of furnace, this slow circulation is not due to magnetic effect, as molten steel is not influenced in this way by the passage of current, but due to the heat generated by the resistance of the lining of the furnace to the flow of current. This causes ordinary convection currents, similar to what is experienced when water is boiled. The hot metal rises to the top and cold metal takes its place. I have seen many hundreds of heats of high-speed steel made in this type of furnace without any mechanical stirring. I think the electric furnace stands pre-eminent in being able to produce a high-speed steel free from occluded gases, oxide, etc., and would like to ask Mr. McKenna his experience on that point.

MR. MCKENNA: There is no doubt that high-speed steel made in an electric furnace, if properly and carefully made, is freer from sonims or soluble metallic impurities than steel made by

[4] General Electric Co., Schenectady, N. Y.
[5] President, Electric Furnace Construction Co., Philadelphia, Pa.

crucible process. High-speed steel made in an electric furnace without using precautions and not under the supervision of a melter trained in crucible practice will contain more sonims or soluble metallic impurities than steel properly made by the crucible process. Whether an average high-speed steel made by the crucible process is as free from sonims as high-speed steel made by the electric furnace process, I cannot say. I can simply say that with good practice, high-speed steel made in an electric furnace contains less soluble metallic impurities than it is possible to reduce them to by crucible process. Occluded gases in high-speed steel give the manufacturer very little trouble.

F. J. RYAN[6]: I refer Mr. Brooke and Dr. Richards to a new type of induction furnace which has been designed and is being manufactured by the General Electric Company at its Pittsfield works.

I believe that in this type of furnace they have overcome many of the objections that originally existed in the induction furnace, especially referring to the single ring which is the principal part of the present furnace development.

I believe that they have also overcome the objections usually existing in the impossibility of getting at all parts of the hearth. Through a special system of doors, all parts of the hearth of this furnace can be reached without any great difficulty.

I have had the opportunity of thoroughly inspecting this type of furnace, both when it was operating and not operating. The manual handling of it is very simple and the special type of refractory that has been developed seems to stand up exceptionally well.

On account of the single-ring design it is impossible to change the cross-section of the bath by tilting and therefore set up internal current conditions which tend to give a stirring action.

Referring to the objection of Mr. Brooke that it is very hard to handle the roof of an induction type of furnace, I would state that in my opinion if all of the furnaces are constructed along the same lines as the small one I have had the opportunity of inspecting, there will be no difficulty in removing the roof or in handling it. It can be handled just as easily as the average type of electric furnace, and in some cases very much easier.

[6] American Metallurgical Corp., Philadelphia, Pa.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

PROPERTIES OF FERROSILICON.[1]

By F. A. Raven.[2]

Abstract.

The various grades of commercial ferrosilicon are described and their metallography and physical and chemical properties discussed. Their production by reduction by carbon in the blast-furnace is described, and then their electric furnace production. The raw materials of the industry, methods of mixing and charging, type of furnace, arrangement and changing of electrodes, slag formation, power consumption, tapping, sorting and grading of products, are severally discussed. Analyses, cost of manufacture and uses of the products are also reviewed. The author declares that furnaces with high frequency current (60 cycles), will work just as efficiently and satisfactorily as low frequency furnaces (25 cycles), if properly designed and operated.

[J. W. R.]

Ferrosilicon always has a crystalline structure. If its silicon content is less than 20 percent it has a dull fracture, shows a fine crystallization, and resembles white iron. With a silicon content of 20 to 30 percent the crystals become more brilliant and show a slaty crystallization. With silicon content of 50 percent or more, the crystallization disappears and is replaced by a fine texture resembling metallic silicon more and more. It is not difficult to judge the percentage of silicon by the eye, according to the texture and the color of the fractured surface. As the percentage of silicon increases to more than 50 percent the ferrosilicon takes on a bluish color.

The various grades of commercial ferrosilicon are substantially

[1] Manuscript received March 8, 1920.

[2] General Manager, Canadian Ferro Alloys, Ltd., Watervliet, N. Y.

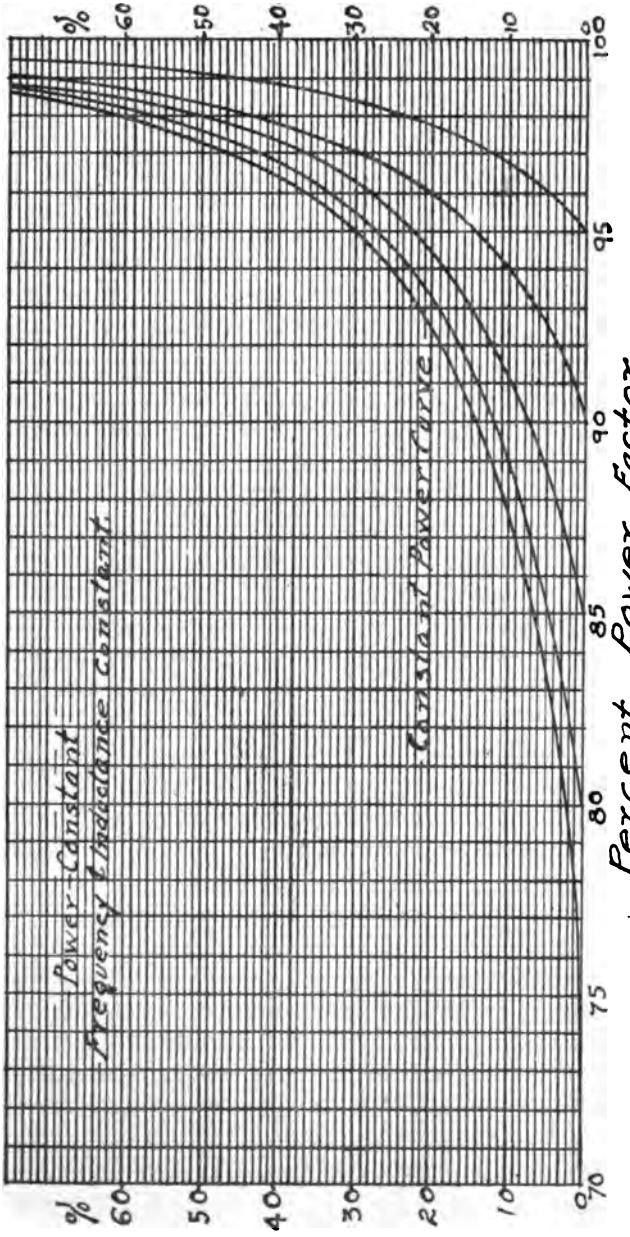

FIG. 1. Relation between Voltage and Power Factor.

binary alloys. Two silicides of iron exist, *viz.*, Fe_2Si and FeSi. The microstructure indicates two eutectics, one containing 24 percent silicon (Fe_2Si and FeSi) and the other containing 60 percent silicon (FeSi and Si). With a silicon content of less than 20 percent the alloys consist of solid solutions of Fe and Fe_2Si, which are hard, firm masses giving off little or no gas. Alloys with a silicon content of 20 to 25 percent silicon consist of primary crystals of Fe_2Si in a ground mass or eutectic composed of Fe_2Si and FeSi. These alloys are more brittle than the lower grades. With a silicon content of 25 to 33.3 percent, the structure shows FeSi surrounded by the eutectic FeSi and Si. With more than 60 percent of silicon there exist silicon crystals in a field of the eutectic FeSi and Si.

The specific gravity decreases as the percentage of silicon increases, because the specific gravity of pure iron is 7.8 whereas that of pure silicon is 2.49.

REDUCTION BY CARBON.

Ferrosilicon is made commercially in two ways only—by the reduction of silica and iron ore by carbon or by the reduction of silica only by carbon the iron being added as iron turnings, which are simply melted.

Silica is reduced by solid carbon at a temperature of 1485° C. The reduction point of silicon is lowered if there is iron present in the charge to combine with the silicon. In commercial practice the presence of iron to lower the reduction temperature is important, as is shown by the fact that furnaces working upon a low-silicon product, with a large charge of iron, operate better than when treating a high-silicon product with a low-iron charge.

Reduction takes place according to the formula:

$$SiO_2 + 2C = Si + 2CO$$

Thus, the reduction of 100 parts of silicon from 214 parts of silica requires 86 parts of carbon. The reduction of iron oxide is generally by the solid carbon only, according to reaction:

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

By this formula, for the reduction of 100 parts of iron from 143 parts of hematite 32 parts of carbon is necessary.

MANUFACTURE OF FERROSILICON IN THE BLAST FURNACE

Ferrosilicon of less than 20 percent silicon is made in the blast furnace, whereas the electric furnace is used for all the grades containing a higher percentage. The grades made in the blast furnace contain 10 to 20 percent silicon, most of them containing less than 15 percent silicon. Higher grades cannot be produced in the blast furnace because of the impossibility of obtaining a high enough temperature. The wear on the furnace lining is great, and in order to maintain the high temperature necessary, a large quantity of coke is employed. As in the electric furnace,

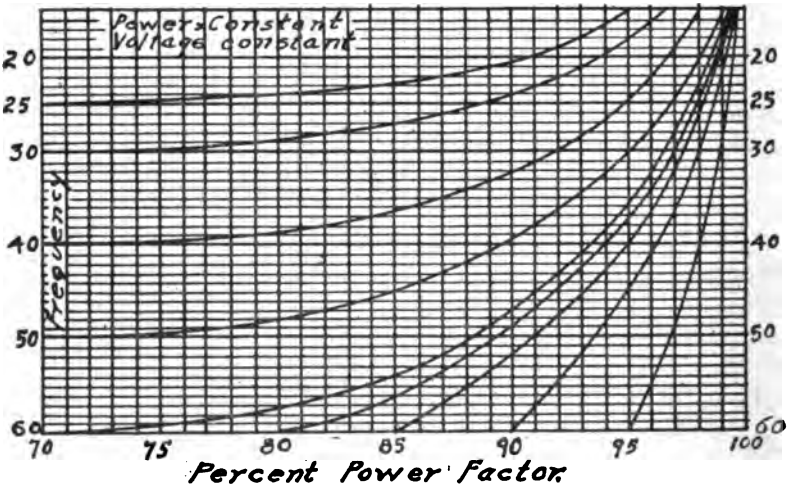

FIG. 2. Relation between Frequency and Power Factor.

the silica is reduced by solid carbon. Reduction is said to be more easy if the slag is low in lime and high in alumina—probably because the silicon does not have as strong an affinity for alumina as for lime. The charge used in the blast furnace may consist of siliceous iron ore, hammer scale and coke, a hot blast being used.

MANUFACTURE OF FERROSILICON IN THE ELECTRIC FURNACE.

Raw Material Used.

There are two general kinds of charge used in the manufacture of ferrosilicon in the electric furnace. The charge may consist

of wrought iron, cast iron or steel turnings, quartz or sand, and charcoal, coal or coke; or siliceous iron ore, quartz or sand, and charcoal, coal or coke may be used. The choice of the source of iron depends chiefly on the material available. Iron in the form of turnings of some sort is more commonly used than iron ore. The operation of a ferrosilicon furnace operating on turnings is much steadier and requires less attention because there is not as much slag formed as in the ore process. The purer the raw materials the purer is the product obtained. For this reason wrought iron or steel turnings are preferable to cast iron borings and are used by most works.

For the supplying of silicon in the charge, quartzite is preferable to sand because it is more nearly pure, and hence does not cause the formation of as much slag, which clogs the furnace. Also, the fine state of the sand seems to cause less regular operation of the furnace. The quartzite is usually crushed to about 2 inch (5 cm.) size. The quartzite charged contains 95 percent SiO_2, 4 percent Al_2O_3, and traces of lime and phosphorus.

Whether charcoal, coke or coal is used depends largely upon the cost of those materials in the district where a given plant is located. As the materials are used only as reducing agents and as, because of the absence of a shaft, no compressive strength is necessary in the fuel to support the charge in the ferrosilicon furnaces, the cheapest reducing material available is used.

The slag increases the difficulties of operation considerably in the production of high-grade ferrosilicon and also increases the furnace impurities that would pass into the product.

In almost all plants the purest raw materials available are procured for making ferrosilicon. As already mentioned, the introduction of slag-forming material into the charge is thus prevented, and the presence of objectionable impurities such as phosphorus and sulphur in the product is avoided. With raw materials containing bases, the silica intended for the product combines with the bases to form slag with such a high percentage of silica as to be very sticky, so that the pieces can be removed from the furnace only by fishing them out as they work to the surface around the electrode, although some of the slag may be tapped with the ferrosilicon. Owing to the strongly reducing nature of the process,

most of the phosphorus and sulphur charged goes into the metal. The sulphur, however, is slagged to a small extent.

Method of Charging.

The raw materials are all thoroughly mixed before being charged into a ferrosilicon furnace. Charging may be from the tapping floor by a man shoveling the charge into the top of the furnace, or charging may be from a floor at the furnace top, the

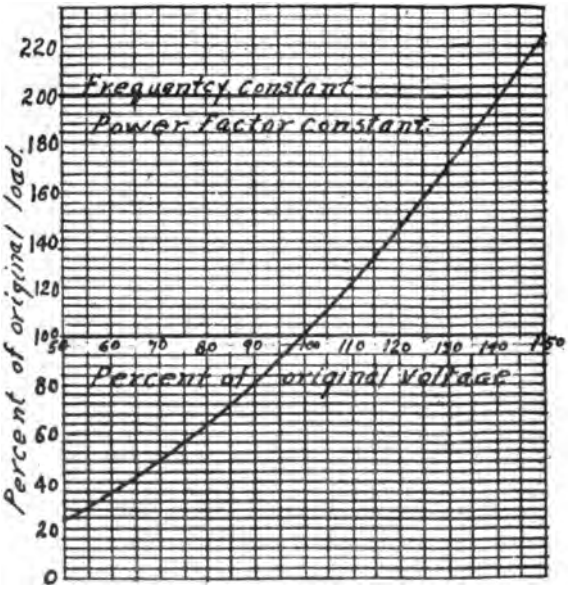

FIG. 3. Relation between Load and Voltage.

usual arrangement in modern works. In charging, the material is placed at intervals around the electrodes, so that the top of the furnace never contains molten material except when some works up around the electrode. The electrode projects about 1 foot (30 cm.) into the charge, and around the end the material is molten and maintains a space of a fraction of an inch (1 to 2 cm.), so that the arc is maintained in the gas formed in this space. The arc is called a free-burning arc. By this method there is a lower power consumption than if the furnace is operated as a resistance

furnace entirely. It is essential that the top of the furnace be covered with unmelted material, so as to cause less electrode and raw material consumption. By operation with a covered bed of fusion, the silicon which is volatilized at a temperature higher than 2000° C. is condensed in the upper part of the furnace. The unmelted charge above also causes the carbon consumption to be lower.

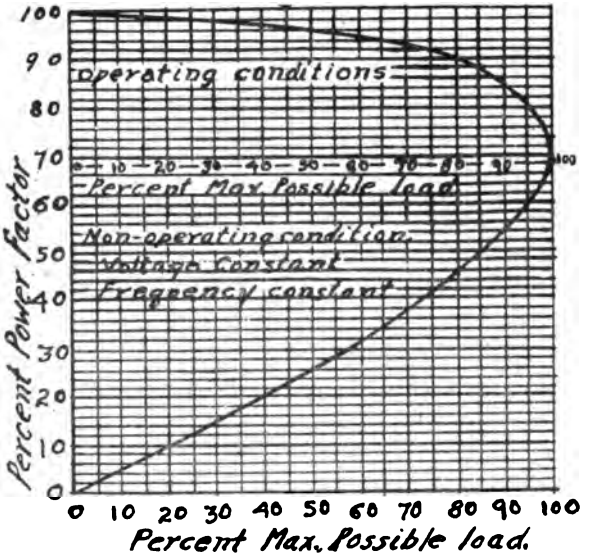

FIG. 4. Relation between Load and Power Factor.

Tapping.

The furnace is tapped as seldom as possible. The necessity of tapping is indicated by the irregularity of the current as shown by the meters and the irregular blowing of gas out of the furnace, also when the metal has been too close to the electrode there is an intermittent pounding sound. The shortest interval is about two hours. The length of the intervals depends upon the percentage of silicon in the product and the size of the furnace. In tapping, an iron rod is driven into the tap hole. If material with a high percentage of silicon is being made, it is sometimes necessary to attach the rod to the circuit and burn out the hole with

an arc. The tap hole is plugged with fine clay or some similar refractory material.

A furnace operating steadily in making ferrosilicon has white fumes of silica passing off at the top, with carbon monoxide burning to dioxide around the electrodes. In some laboratory experiments by the writer, the condensed fumes from a ferrosilicon furnace contained 67.69 percent SiO_2, 9.72 percent Al_2O_3, 4.11 percent FeO, 0.20 percent MgO and 1.90 percent CaO, the rest probably being carbon.

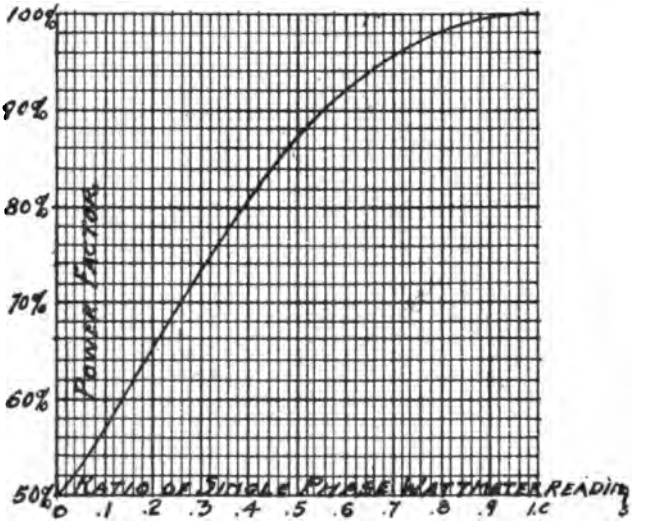

FIG. 5. Determination of Power Factor of Balanced 3-phase Loads by Use of 2 Single-phase Wattmeters.

Changing Electrodes.

Electrodes are replaced by simply swinging one in over the furnace, replace the holder and remove the burnt electrode. If the electrode has a tendency to rise in the furnace when a fixed voltage is being maintained by hand regulation of the electrode, quartz, a relatively poor conductor is charged around the electrode, so that it becomes necessary to lower the electrode to maintain the current steadily. If the reverse is the case, carbon is added to put in a good conductor for raising it.

Slag Formation.

Because of the use of pure raw material, comparatively little slag is formed in a ferrosilicon furnace. The slag formed consists of silicates of alumina and lime or magnesia. They are very high in silica and are rather infusible. The addition of more basic material to make them fusible would do no good, because it would simply draw more silica from the charge and increase the total slag. As the percentage of silicon in the product increases, the specific gravity of the product decreases so that it is difficult to obtain separation of slag and metal if the slag is sticky. In the manufacture of the 25 percent alloy, slag is permissible; with a silicon content of 50 percent operation is difficult, and with higher percentages is impossible if slag is present. As a rule, these slags are so thick that they are not tapped, but boil up around the electrode and are removed there. The results of some analyses are as follows:

	Sample 1 Percent	Sample 2 Percent	Sample 3 Percent
SiO_2	68.86	67.60	79.25
Al_2O_3	13.80	19.63	9.04
CaO	26.40	17.00	19.17
Fe_2O_3	1.96	1.02	3.50

The ferrosilicon is tapped into cars lined with sand or carbon. It is dumped to cool, and broken into small pieces with hammers and weights. In tapping, iron must be kept away from the molten ferrosilicon, because in the molten condition it dissolves iron readily. The product is usually packed in barrels or boxes, or shipped loose.

Power Consumption.

The power consumption on a 7500 K.W. furnace was 5950 K.W. hours per long ton (1016 kg.) of 50 percent ferrosilicon. Of the total energy 64 percent was usefully used, 9.0 percent was used in volatilizing silica, 0.20 percent in volatilizing iron, and 26.80 percent was lost by induction, radiation, and other losses. The electrode consumption during a month of steady operation averaged 84 pounds per long ton (38 kg. per metric ton) of 50 percent product. Amorphous-carbon electrodes were used.

Products.

Electric furnace ferrosilicon is produced in grades classified according to silicon content, which are as follows for each grade: 45 to 50 percent, 75 to 80 percent, and 90 to 95 percent. The selling of these products is based entirely upon the silicon content, because the carbon content, owing to its usual low percentage, has no effect upon the price, as in other alloys. Below are given the analyses of the three grades of electric furnace ferrosilicon:

Constituent	Silicon Content		
	45 to 50 Percent	75 to 80 Percent	90 to 95 Percent
Silicon	49.50	78.00	88.50
Iron	49.00	20.00	9.30
Manganese	0.30	0.25	0.15
Aluminum	0.15	0.10	0.15
Magnesium	0.15	0.30	0.30
Carbon	0.30	0.30	0.25
Sulphur	0.015	0.015	0.015
Phosphorus	0.03	0.03	0.03

Cost of Manufacture.

The cost of manufacture of ferrosilicon depends more upon the price of electric power than upon any other item. This is because of the large amount of power necessary and the low cost of the raw material composing the charge. Consequently a large part of the electric furnace ferrosilicon used in the United States is imported from Europe and Canada.

The electrode consumption is based upon the use of electrodes threaded for continuous feeding, a practice now universally followed in ferro-alloy plants.

Uses.

The chief use for ferrosilicon is for the deoxidation of steel by the formation of silica or silicates with any free oxygen or oxides, the silica or silicates thus formed passing into the slag. A considerable amount is used for making fixed additions to steel. The grade containing 25 to 30 percent silicon is used as a substitute for blast-furnace grades containing 10 to 12 percent silicon.

It is especially useful for direct addition to the open-hearth furnace, the cupola, or the converter, but may be added in the ladle. It is compact, in large pieces, and of sufficient specific gravity to sink readily in the bath. It reacts more energetically than does the alloy with the lower percentage of silicon and the quantities employed need not be so large. This grade is used chiefly for fixed additions of silicon.

Ferrosilicon with 45 to 50 percent silicon is employed particularly for deoxidation. It reacts like the 25 to 30 percent alloy but more energetically, and is used when the greater specific

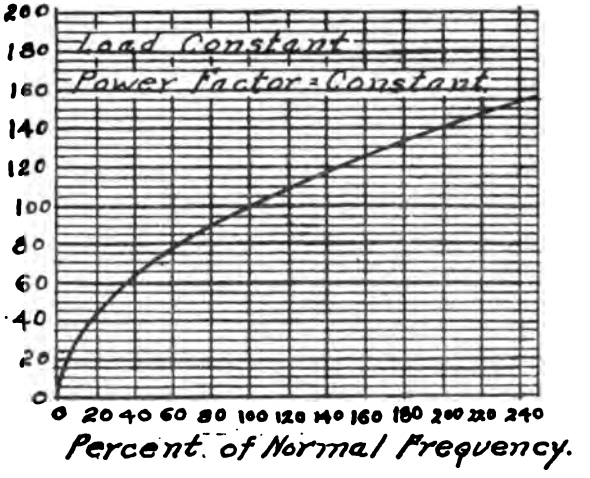

FIG. 6. Relation between Frequency and Voltage.

gravity of the latter is not essential. It has a lower fusion point than the lower grade. It is subject to disintegration, and is the only grade from which poisonous gases have been known to emanate. It is used in greater quantity than any of the other grades.

The grade containing 75 percent silicon is employed for additions to ordinary castings. It can be used to modify a casting so as to obtain either a white or a gray casting, by addition to the casting ladle. For a fixed addition in the production of silicon steels, such as transformer steel, 75 to 90 percent ferrosilicon is employed.

A great deal has been said and written about the impracticability of operating large furnaces on high frequencies. It has been

the experience of the writer that a sixty-cycle furnace of large capacity properly designed electrically and otherwise and properly operated can be made to produce just as efficiently as one of low frequency. Of course the same design and practice used on a twenty-five cycle furnace cannot be used on a sixty-cycle furnace. It would take up too much time and space in this article to get into details of the different layouts for different frequencies.

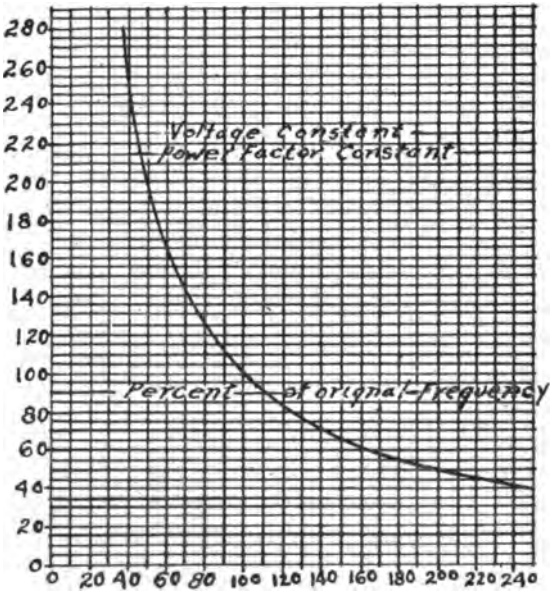

FIG. 7. Relation between Load and Frequency.

The writer has operated furnaces both large and small on twenty-five, forty, and sixty cycles, and has been able to produce practically the same results on all three frequencies. Attached hereto is a set of curves which the writer has used in the layout of the electrical end of the alloy plants. This set of curves is self-explanatory.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

DEVELOPMENT OF FERRO-VANADIUM METALLURGY.[1]

By B. D. Saklatwalla.[2]

ABSTRACT.

A general review is given of the occurrence of vanadium in nature, its discovery and its restricted utilization as a rare and expensive element. Details are then given of its modern introduction into large scale metallurgical practice, in armor plate and special steels. Finally, extensive details are given of the reduction of its compounds to metal by silicon in the electric furnace, and of the alumino-thermic reduction as practiced on a large scale in this country. The attempts to produce the pure metal, free from carbon, are also considered and their difficulties discussed.

[J. W. R.]

We will discuss briefly the technical evolution of the processes of reduction, and the general properties bearing on such processes, of an element which up to only a few years ago was characterized as a chemical curiosity, a so-called rare element. Following a recognition of its useful properties, this element, "vanadium," was suddenly converted from its laboratory obscurity into a commercial necessity of far-reaching importance. In this commercial evolution it resembles, to some extent, the element aluminum, which was similarly transformed from an element of chemical catalogs into a metal of everyday necessary technical and domestic use. Vanadium, like aluminum, destined to be a great engineering factor, was known to exist, and its chemistry fairly well developed, years ahead of its actual entry into commerce.

This neglect of its useful properties was due to various substantial reasons. In the first place, its technical uses were limited

[1] Manuscript received March 22, 1920.

[2] General Superintendent, Vanadium Corporation of America, Bridgeville, Pa.

until Prof. Arnold's researches conclusively proved its value in the manufacture of steel; hence there was very little incentive for its technical development. In the second place, though its presence was widely manifested, it was of rare occurrence in a commercially workable deposit. Vanadium had been classed among the rare elements, with very little justification. It was not the distribution of the element, but its occurrence in a concentrated form at one locality that was lacking until the discovery of the Peruvian deposits in the Andes, near Cerro de Pasco, by Don Antenor Rizo Patron, in 1905. In fact, vanadium is one of the most widely distributed elements on the face of the earth. It is diffused through all primitive granites and many sedimentary rocks and clays. Besides forming a number of special minerals, its presence has been proved, as accompanying other elements, in at least fifty different minerals. In large amounts it occurs in lead ores, and in very small quantities in iron and copper ores. It is found in the ashes of very many coals and various plants. Its distribution as to locality also is not restricted, none of the continents of our globe being free from it. To get an idea of the quantity of vanadium contained in our globe, Vogt comes to the conclusion from various quantitative determinations in minerals, that the entire crust of the earth would show an average content of between 0.0025 and 0.05 percent vanadium. Further, the presence of vanadium is not restricted to our planet alone. Sir Norman Lockyer has shown its presence in the spectra of various heavenly bodies. Also a number of meteorites have been shown to contain vanadium.

The history of vanadium is more than a century old. It was discovered in 1801 by Manuel del Rio, in the lead ores of Zimpan in Mexico, but was considered by Collet Descotils, who analyzed these ores in Paris, to be identical with chromium. Thus del Rio's discovery was forgotten, until Sefstroem, in 1830, re-discovered the element in iron produced from certain Swedish ores. Then Woehler, taking up the analysis of the Mexican lead ores investigated by del Rio, conclusively proved that Sefstroem's new element was the same as that found by del Rio, *viz.*, vanadium. This controversy inspired Berzelius to investigate the chemistry of this new element in a most thorough manner. It will not be too much to say that the foundation on which the chemical knowl-

edge of this element is erected is formed by the work undertaken by this old master in 1831. Comparatively little was added to it, until Sir Henry Roscoe, about 40 years later, through his researches from 1867-1870, furnished additional valuable data. The first suggestion of technical application of vanadium to metallurgy carries us back to the year 1863, when Lewis Thompson expressed the idea of vanadium having a similar effect to nickel on iron, since it was found in iron of remarkable ductility. A year later, Edward Riley suggested the extraction of vanadium from pig iron, which being analyzed by him, seemed to contain this element.

The treatment of vanadium-bearing materials and minerals can be said to have started following Roscoe's work in 1867-1870, when vanadium found application in the dyeing and ceramic industries, but it was not until 1896 that its entry into metallurgy can be said to date. In that year the Firminy Steel Works in France experimented with the use of vanadium in armor plates. However the superiority of vanadium steels cannot be said to have been established until the year 1900, especially by the comprehensive investigations of Prof. Arnold in Sheffield, England, which work was further completed by the publication of Sankey and Smith in 1904. Immediately after these publications, establishing the usefulness of vanadium in steel metallurgy, the most important known deposit of vanadium-bearing mineral was discovered in Peru in 1905, thus ensuring a permanent supply for the establishment of a vanadium industry and a commercial technology for the treatment of vanadium minerals.

Owing to the general low metallic content of vanadium-bearing minerals and the presence of comparatively very much larger amounts of other elements in such minerals, all processes for the reduction of the metal were, at the beginning of the industry, preceded by a chemical separation of the vanadium content. Such separation was effected by dissolving the vanadium away from the other constituents, and then obtaining it out of such solutions in the form of an oxide, by evaporation and calcination or by precipitation. The precipitated oxide was then usually fused and ground, and formed the material which was subjected to the process of reduction for obtaining of the metal. This chemical separation by a wet method was naturally attended by a long, costly and wasteful operation. In the treatment of the Peruvian patron-

ite deposits, owing to their comparatively high vanadium content, it was possible to eliminate all wet treatment and develop a purely metallurgical dry smelting process, with its attendant facility of operation and great saving through elimination of losses. This meant a very great advance, in view of the scarcity and costliness of an element like vanadium.

In spite of the widely-scattered occurrence of vanadium, its commercially workable sources are restricted to the patronite formation of Peru and the roscoelite deposits of Colorado. Besides these the carnotite deposits yield a small tonnage as by-product in the extraction of radium.

The roscoelite is treated by roasting the ore with salt and pyrite in a Wedge furnace. The calcined ore is then leached with hot water and the dissolved vanadate is precipitated by ferrous sulphate as iron vanadate, which, after being filtered and dried, is subjected to the reduction process. In the case of carnotite ores the vanadium is extracted as a by-product by similar chemical reactions.

In the wet extraction of patronite ore, which is a vanadium sulphide, it is subjected to a preliminary roasting to eliminate the sulphur, after which it is treated with sulphuric acid, to dissolve the vanadium as sulphate. The sulphate liquor is either evaporated to a sulphate cake, which is calcined to the oxide, or the sulphate solution is treated with oxidizing agents, such as oxy-acid compounds of chlorine, which cause precipitation of the vanadium as vanadic acid. This precipitate is filtered, dried, and reduced to metal.

In the more recently developed treatment of patronite ore by dry metallurgical means, the ore is subjected, after addition of fluxes, to a matte smelting in a reverberatory furnace. The matte carries all the heavy metal constituents of the ore such as iron, nickel, molybdenum, any copper, traces of arsenic or antimony, if present in the ore, leaving a supernatant slag containing the entire vanadium content combined with all gangue material, such as silica, lime, alumina, magnesia, etc. This slag, forming more or less a glass, is granulated in water, dried and subjected to a reduction process, the separation of the gangue being effected by suitable fluxes in the process of reduction.

Before discussing the rationale of the reduction processes themselves, it would be advisable to enter into a few theoretical considerations forming the basis of such processes.

The element vanadium stands in the periodic system in the fifth group of elements, with nitrogen, phosphorus, arsenic, antimony, and bismuth, between phosphorus and arsenic. Moreover, its atomic weight lies between that of titanium and chromium. Owing to this position, it shares the characteristic property of these elements of showing different valencies, and functioning as a basic as well as an acid-forming element. Like nitrogen, it shows at least four different valencies, and with decrease of valency an increased basic tendency. This fact plays an important part in the reduction processes, as, generally, the starting material for reduction is a vanadium compound of high valency and of consequent high acidity, namely V_2O_5, which in the reduction process goes through successive decrements of valency and acquires more basic properties. Consequently in the calculation and selection of flux and slag-forming materials this fact has to be kept in mind. This factor plays an important part in determining the losses suffered in reduction through retention of the vanadium in the slag, combination with furnace lining, etc. Also the great combining activity of vanadium with all other elements, especially with oxygen, is a similar factor. In practice it has been found that the best means to offset any detrimental effects of these factors is to accomplish the reduction instantaneously, not allowing time for any such secondary combinations or re-oxidations. The temperature at which reduction of vanadium from the oxide is effected appears to be rather high, and the problem faces us of producing this high degree of temperature in the reduction zone in as short a time as possible. These considerations will easily show us why the alumino-thermic method of reduction has played such a great factor, commercially, in the reduction of vanadium. It is probably the only commercial metallurgical operation where aluminum has been used as a reducing agent to such a large extent, and where the technique of alumino-thermic reduction has been developed to such a high degree of perfection on a large scale.

Aluminum very conveniently presents a concentrated form of energy, in a transportable form, ready at an instant's notice to

make itself available. It is nothing more or less than an accumulator of the electrical energy expended in its own reduction. In reality, therefore, the reduction of vanadium is effected indirectly by electrical means, as the aluminum represents nothing else than the electrical energy which was expended in its own reduction, conveniently transported and still more conveniently applied. As in the case of the properties of vanadium, so it is with its largely used method of reduction, that a knowledge, existing for a long period of time, was not commercially taken advantage of. The process of reducing metals by aluminum had been known for years before the advent of vanadium, but had not been transferred to commercial technology. In the reduction of vanadium by aluminum this art has been developed in late years to such an extent as to practically constitute a new branch of metallurgy.

In the aluminum reduction to ferro-vanadium of practically pure vanadic acid or iron vanadate prepared by the wet process, the technique of reduction is as follows:

The material in a crushed or granulated form is mixed with grained aluminum and the necessary amount of iron scale, or iron turnings, and fluxes, such as borax and fluorspar, the latter to increase the fluidity of the slag and effect a better separation of the metal from it. This mixture is fed by means of a mechanically operated screw feeder into a magnesite-lined iron crucible standing in an enclosed chamber. This crucible is preheated to a red heat, and the ignition of the mixture is started by a small quantity of so-called ignition mixture, consisting of grained aluminum and sodium or barium peroxide. When this ignition mixture has deflagrated from the heat of the crucible, the requisite temperature for ignition of this mixture being approximately 550° to 600° C., the reduction mixture is fed in, which in turn reacts at approximately 1000° to 1100° C. The rate of feeding the mixture is kept, for best results, as nearly as possible to the rate of reaction of the mixture. The pre-heating of the crucible and the rate of feeding have great influence on the results obtained, as they affect the temperature produced and consequently influence the fluidity of the slag and its separation from the metal, allowing it to gather in a homogeneous reguline mass. Another factor which greatly affects the velocity of the reaction and thereby the results obtained, is the size of grains of the ingredients of the reducing

mixtures. We have to bear in mind the fact that this reaction is carried on without any extraneous heat being applied to the mass, and that the heat requisite for the reaction and for the melting and heating of the products of the reaction is produced by the reaction itself. In other words, we are dealing with an exothermic, self-propagating reaction. Consequently, the temperature vitally governing the results obtained will be dependent on the amount of heat liberated by the reaction per unit of time. Naturally this will depend on the area of the interacting surfaces of contact of the solid ingredients entering into reaction and the velocity with which these reacting surfaces are fed into the reaction temperature zone. Hence can be clearly seen the effect on the commercial results obtained by controlling the size of granulation of the ingredients of the mix, the distribution of same over the reacting area, and the velocity of its feed. Under this mechanism of the process the liberation of the energy of the aluminum and its useful application are brought under perfect control and technically harnessed, and not left to chance, as in the application of other aluminum reductions, where the entire mass of the reacting materials is filled in a crucible and subjected to reacting temperature, either at one point, or over the whole crucible surface by placing it in a furnace. The crucibles for such vanadium reduction were of dimensions as to produce a button of alloy weighing from 100 to 150 lb. (45 to 68 kg.), several such crucibles and chambers with feeding mechanisms being used to produce one heat of the alloy.

The increased demand for ferro-vanadium in industry necessitated a large output, and, naturally, attention was turned to methods of manufacture suitable for large-scale operations. The leaching processes would demand a very large equipment for a comparatively small tonnage, so would also the method of reducing in small individual crucibles. Experiments were made to carry on the reduction by means of aluminum in furnaces. Several types of hearth furnaces were tried out and used, including combinations of shaft and hearth furnaces where the reduction was carried on in the shaft and the hearth used as a collector or fore-hearth for accumulation and separation of the products of reduction. The resulting metal and slag were tapped from time to time. It was, however, found that best results were obtained

by the use of a vertical shaft furnace, lined with a suitable refractory, and provided with adequate spouts for tapping the alloy and the slag. The shell of the furnace was divided vertically in two halves and bolted together in order to facilitate removal of the old refractory lining and renewing it with fresh material. These shaft furnaces have a height of 9 ft. 3 in. (2.8 m.) and a diameter of 4 ft. 6 in. (1.35 m.). One of these furnaces with a single lining is capable of producing approximately 125,000 lb. (57,000 kg.) of alloy per run. The advantage of this method can readily be seen when we recollect that the individual crucible with one lining produced only about 150 lb. (68 kg.) of alloy. Further the alloy being produced in large quantities and tapped into large ladles, several thousand pounds at one tap, has the advantage of being more uniform in composition. This operation undoubtedly shows the advance made in this technique when we compare these quantities with the few pounds generally produced in small magnesite-lined graphite or iron crucibles used in previous operations for reducing other metals by aluminum.

The results obtained in the large furnaces were not only different from the crucible operations in magnitude, but, owing to large quantities of reduction mixture interacting at one time and accumulating the heat in the furnace walls from tap to tap, very much higher temperatures could be produced than was possible in a small crucible. The temperature produced has been estimated in the neighborhood of 2500° to 2800° C. This increased temperature had a very beneficial effect on the formation and fluidity of the slag and also on the separation of metal and slag. A much greater advantage of this increased temperature was the fact that it made possible the reduction of a compound which was not a pure oxide but a complex mixture of silicates and double silicates, such as the slag from the matte-smelting operation or the sulphide ores. It was possible, owing to the higher temperature in the shaft furnace, to add suitable fluxes to form a slag with the oxide of the elements which were not desired to be reduced into the alloy. Thus a refining and complex slag-forming operation requiring absorption of heat energy could be carried out, which was not possible to accomplish in the small crucibles. In

this connection we should recall the fact that the temperature to be produced has to be controlled by the proportions and nature of the active ingredients of the reducing mixture itself, and any additions of slag-forming fluxes would absorb the heat energy produced, and thus retard the main active reaction. Thus it was possible to effect the separation of vanadium from the gangue material, which was accomplished in the older processes by leaching, in this process, simultaneously with the reduction operation by utilizing the heat energy which was produced, whether such separation was to be effected or not. Also in this operation, just as in the case of crucibles, the velocity of the reaction is controlled by the rate of feed, size of granulation, chemical nature of the flux ingredients of the mix, etc.

We have previously seen that the chemical energy of the aluminum in the process of reduction is only an indirect application to reduction of vanadium of the electrical energy consumed in the isolating of the aluminum. Naturally one would think of applying electrical energy directly to the reduction of vanadium, without the intervention of an intermediate product. Already in the early days of the ferro-vanadium industry, an electric smelting process was developed. This process consisted in reducing vanadium oxide by means of silicon in an electric furnace. The silicon was used in the form of the 90 percent metal or as 50 percent ferro-silicon. This process was successfully used for commercial operation. Naturally this process is associated with the disadvantage, similarly to the case of the aluminum reduction, of utilizing a costly reducing agent.

The reduction of vanadium by means of carbon in an electric furnace has been, however, a more difficult problem, and has only recently been successfully solved and put into commercial operation for the past three or four years. We will be able to understand this difficulty when we recall some of the facts mentioned at the beginning of this paper. We have mentioned that the reduction of vanadium requires a high temperature and that this reduction has to be effected in as short a period of time as possible. The aluminum reduction was successful because it produced these conditions. The reduction was effected instantane-

ously, the high temperature being produced right in and by the mass to be converted to a fluid condition, as soon as the mixture was brought into the zone of reacting temperature. The silicon reduction, in the electric furnace, was successful because there was generated by the reaction a quantity of heat, and consequent temperature within the mass to be melted, though not to the extent of aluminum. This lacking difference in energy, however, was made up by the electric energy put into the furnace. In the carbon reduction this evolution of heat through the reaction is not present, as in the case of the metallic reducing agents. A very high temperature zone has, therefore, to be produced by the extraneous electrical energy alone, inside the furnace, right in the reducing mass, preferably close to the top of the metal bath, and the reacting mixture has to be fed directly into this zone so that the reaction can take place as quickly as possible.

By the realization of these conditions, very analogous to the physical conditions in the aluminum reduction, produced by the application of a high voltage current and a high current density, and close spacing of electrodes to localize the heat, it has been possible to very successfully reduce vanadium-bearing materials by means of carbon, producing a product of good commercial quality suitable for all metallurgical purposes. For the localization of the arc at the proper zone in the furnace, several ore mixtures have been developed which possess the requisite electrical properties in the molten state to permit the electrodes being dipped to the right depth in the molten bath. The furnace used for the purpose is a three-phase rectangular furnace, with a water-cooled cover, furnished with water-cooled bushings for three 12-inch (30 cm.) graphite electrodes. The mix is fed in the furnace through water-cooled bushings in the top of the cover by means of continuous automatic feeders. The mixture of ore, coke, and fluxes is fed in a finely-divided state and thoroughly mixed. The furnace is tapped at an interval of approximately every six hours for metal and slag.

One fact in connection with the electric reduction of vanadium is worth mentioning, namely, that the first ferro-vanadium alloys manufactured commercially were reduced electrically, with silicon

as reducing agent, and, undoubtedly, the bulk of the future commercial output is to be produced electrically with carbon as reducing agent. Already a very large proportion of the commercial alloy is produced in this way.

After reviewing the reduction processes for the manufacture of vanadium in the form of alloy it will not be out of place to mention here the attempts at reduction of the metal in the pure state. It might be well to mention at the start that this has up to now never been accomplished, and is one of the most difficult problems of experimental chemistry. On account of the great combining power of this element with most others, the ordinary methods of preparation of the pure metal have met with very little success. The reduction of the oxide by means of hydrogen, or electrolysis in the molten state, as well as electrolysis of aqueous salt solutions, have failed. Reduction with aluminum has been unsuccessful, never giving a product higher than about 93 percent pure. Roscoe's claim to have produced the pure metal by reduction of the chloride in a stream of hydrogen is restricted to a product of little over 95 percent vanadium. Reduction with "Mischmetal," a mixture of cerium and yttrium-group metals, is claimed to have produced a perfectly pure metal, though no analysis of the product obtained is given. Further, Werner von Bolten claims to have obtained pure vanadium by heating to glowing, by means of an electric current, a filament of vanadium pentoxide sealed in an evacuated glass vessel. Ruff and Martin claim to have produced vanadium up to a little over 98 percent, but containing over 1 percent carbon. It is, however, very doubtful whether by any of these means metallic vanadium has ever been produced which can be said to be practically pure metal.

This difficulty of production of the metal in the pure state will probably account for the introduction of vanadium in the industry in the form of alloys. Technically the ferro-alloys, besides being easier of production, show marked advantages over the metal itself. They possess a much lower melting point and a greater solubility, factors vitally essential to the introduction of the alloy in a steel or iron bath. To further accentuate these properties, in certain cases, additions of silicon and manganese are made

during the production of the ferro-alloy to obtain a composition still lower in melting point and of higher solubility.

In the above resumé we have summarized the present status of manufacture of a material vitally essential as an engineering factor to our present civilization, with the expectation of being able to record, in the future, further advances just as remarkable as those from the period of inception of the industry to the present time.

DISCUSSION.

G. M. BERRY[1]: Those of us who use vanadium have been increasingly aware of the fact that it is getting scarcer. That may be, to some extent, due to the financial control on the part of the producing sources. I do not know enough to make a statement on that point, and do not want to guess but I would like if Mr. Saklatwalla would tell us something of the prospects of having a sufficient supply for the American market in the near future and at a little further removed future.

B. D. SAKLATWALLA: The reason why it is scarce is that the natural deposits are scarce. There is only one known large deposit in the world today, and that is in the Peruvian Andes. These deposits are being developed today to a wonderful extent. It is not that the supply has very suddenly diminished, but that the consumption has so rapidly increased that the mining operations, being situated in such distant countries, have not been able to keep anywhere near the pace set by the consumption. Also the available sources in this country have been investigated during the war, and I think that the geological survey has made a report on it. The sum and substance of that report is that if all the known vanadium available in this country should be put to practical use, it would not supply one-tenth the demand of this country alone, much less that of the allied nations. Consequently the Peruvian deposit has to supply the entire world. As to the financial control, of course, when there is only one deposit of any value to be controlled, why, there could naturally be only one control.

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G. M. BERRY: Dr. Saklatwalla is a diplomat as well as a scientist. There is no question in my own mind about there being one deposit, but the question I am interested in is whether those of us not directly connected with the control of that one deposit are going to be able to get vanadium, that is, whether the whole country is going to have an adequate supply to meet its needs? I want to know about the commercial proposition. Are we going to have vanadium produced from the Peruvian deposits, in your judgment, such that the consumption will be amply taken care of in the immediate future and the more remote future?

B. D. SAKLATWALLA: Yes, it will be well taken care of, very much better than it is being taken care of today or has been taken care of in the past. What I presume you are referring to is that the people who control the vanadium are themselves interested in the steel business, and you want to know whether they are going to reserve that to their own advantage. The people who control the vanadium deposits are in the steel business, but not in the alloy steel business; they will therefore not use vanadium to any great extent. The great demand for vanadium is in the automobile business, and the largest users of vanadium today are not in any way affiliated with the people who control the vanadium deposits. They are infinitesimally small users of vanadium themselves.

G. M. BERRY: I understand that there are physical difficulties in the way of getting the vanadium deposits, such as high altitude, and the average Anglo-Saxon cannot stand it. I understand also that it is brought considerable distances by llama back or Indian back, and my real question is, are the deposits being worked or is there any possibility of getting increased production so as to supply us without having the price continually soar as it is doing at the present time. Tell us something about that; that is what I want to know.

B. D. SAKLATWALLA: Well, you are correct; the deposit is situated at a high altitude, and is hard to reach. It is situated at approximately 17,000 feet above sea level, which is the highest place in the world where any commercial mining operations are carried on, and all the ore transmitted from the mine to the railroad is at present sent on the backs of llamas, and the llamas are

being exterminated in all South American countries. To offset this condition, we are building at the present time a railroad which is in course of construction from the mine. There have been already some truck roads built and there are gasoline trucks being operated. When this railroad is finished, which we expect to in the course of four to six months, the conditions for obtaining a greater supply of ore from Peru will be very much better than they are now. Another thing that we are contemplating and are engineering is to build a sort of a concentrating plant in Peru in order to concentrate the ore at the mines, so that the transportation question, which is the great question today, will be simplified. We expect to concentrate about ten to one, so with the railroad built, the existing truck roads, and with the concentration of the ore at the mine plant, the future for the vanadium supply will be very bright.

G. M. BERRY: Are you able to say, in length of time, how long before that relief ought to come? Are you able to make any prediction?

B. D. SAKLATWALLA: The railroad is going to be finished at the end of the summer. But as for the concentrating plant, while you have mentioned about the altitude difficulties, you have not mentioned about the speed with which operations are carried on in those countries, and naturally while it would take us about four or six months to build a plant in the States, it will take about three years there to do the same thing, and it is, therefore, a pretty hard guess to be able to state any definite time, but it will be, I would judge, within the course of a couple of years.

COLIN G. FINK[2]: This paper of Mr. Saklatwalla is certainly very interesting. To my recollection it is the first contribution on ferro-vanadium that the Society has ever had. Mr. Berry points out that prices have gone up, and the question arises, are we necessarily dependent upon vanadium? Can we not use something else in place of vanadium?

J. W. RICHARDS[3]: I think that the company that developed this splendid deposit down in Peru, overcoming very great natural difficulties and taking great risks in investing their capital, deserve

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[3] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.

a good return for their enterprise. In doing so, however, the history of these rare minerals would lead us to expect, with a considerable degree of surety, that the high price and great demand for vanadium, greater than the supply, will inevitably lead to great exploitation or prospecting in different parts of the world, and since vanadium is so widely distributed, it is very likely that the history of tungsten and other rare metals will be repeated, and that large deposits will be found in the future. I confidently look forward to considerable deposits being uncovered, just because of the great incentive to the finding of such ore. I do not think that the deposit in Peru is the only possible deposit of vanadium in the Andes, and certainly it is found in so many other parts of the world that we may confidently look to a large extension of the supply of vanadium, as has happened with other similar rare elements.

H. W. GILLETT[4]: There is one question I would like to ask in regard to the reduction by carbon. According to the history of vanadium steel it appears that in the early days vanadium steel was first advocated and then generally condemned, and several years elapsed before its value was really understood. It now looks as though a good deal of the difficulty in the early days was due to the use of high-carbon ferro-vanadium, since as far as I can gather from the literature, it appears that vanadium alloys high in carbon are not satisfactory to the maker of steel. I would like to have Mr. Berry tell us about that; at any rate I would like to know the carbon content of the finished alloy made by carbon reduction, whether such an alloy is equivalent to ferro-vanadium made by aluminum or by silicon, from the point of view of the steel man?

B. D. SAKLATWALLA: The reason I do not think that the trouble they had, if any, at the beginning of the industry was due to the carbon content (and I think Mr. Becket will corroborate me, since he knows it) is because the carbon content of the alloys that he produced in the electric furnace was low and there was not any trouble about the carbon at all. What has crept into the literature about the carbides, etc., that they are not soluble in steel is not so. Alloy running 7 percent in carbon has been used

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with just as good results in steel as most of the low carbon alloys. Even the alloy produced for the last four or five years by aluminum reduction carries a high percentage of carbon, for the reason that when the refractory trouble about refractory material started during the war; all vanadium formerly manufactured in magnesite lining was reduced in lining of coke or graphite. Consequently all the aluminum-reduced alloy carried one to one and a half percent carbon. The alloys produced today in the electric furnace do not carry any more carbon than the alloy thus reduced by aluminum in a carbon lining.

H. W. GILLETT: Do you get the same recovery from ferro-alloy to steel?

B. D. SAKLATWALLA: Absolutely.

G. L. NORRIS[6]: I would like to allay the gentleman's fears about the amount of vanadium available in the future, and assure him that he can continue his plant in operation without any fear. As Dr. Saklatwalla said, by August we ought to have the railroad in operation; by that time, or before that time, the way shipments are coming up, we will be able to make prompt delivery of all the vanadium demanded by the steel works, based on the present demand. Now, as to price, I will simply say that during the war the American Vanadium Company maintained practically pre-war prices. This they were able to do because of the enormous stock of ore carried in this country. At the close of the war this stock was practically used up. Since then on account of the greatly increased costs and difficulties of mining and transportation and increased costs of all materials used in production, the price has necessarily advanced, but not proportionately to the advance in other materials.

G. M. BERRY: It has been the experience of all vanadium users, I am sure, that latterly the silicon content of the ferro-vanadium in the market has been very much higher than a few years back. Can you enlighten us as to why that is so?

G. L. NORRIS: In order to meet the demand, we have had to produce the vanadium as rapidly as possible, for one thing. The mining situation in Peru, to which Dr. Saklatwalla referred, has

[6] Met. Engr., Vanadium Corp. of America, New York City.

been very bad; owing to South American mining methods, left largely to native engineers, the mining was relatively crude. The result was that we had a slide that buried our best workings, and we have been over a year now in cleaning them up; meanwhile, we have had to mine and ship a lower grade ore, which was more highly silicious. The natural result was that unless we went to a great deal of expense and increased the cost of manufacture unduly, we had to let the silicon go into the alloy. The silicon in the alloy does absolutely no harm, in fact it can be made a source of gain to the user. It is only in the production by crucible melting of high-speed steel containing over 1 percent of V that high silicon ferro-vanadium cannot be successfully used, as this method of melting does not permit the slagging off of silicon. In the electric furnace, however, it is entirely possible to add one percent of vanadium or more, and maintain a low silicon content in the steel; in the case of the open-hearth furnace steel usually only one-quarter of one percent of vanadium is added, and the silicon content in the alloy is negligible.

G. M. BERRY: Of course you can use high silicon if your product will admit it, but if you have to make a product that requires a lower silicon, if you are hard put and have to seek a lower silicon content in some other material that goes into the mix in order to keep within bounds, you cannot accept more than you can use.

G. L. NORRIS: That applies only to the crucible steel process in which you cannot slag off silicon; in the electric furnace, you can slag off, and you can get rid of the silicon in the ferro-vanadium without losing vanadium. This is being done today and has been done for months.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

FERROCERIUM.[1]

By ALCAN HIRSCH.[2]

It is about nine years since I presented before this society a paper on cerium and its alloys. At that time cerium and its pyrophoric alloys were more or less novelties and curiosities, but today they have grown to be a stable commodity taking their proper place in industry and commerce, and replacing more and more the match. During the recent world war, pyrophoric alloy lighters formed a part of the standard equipment of every soldier, particularly the type of lighter known as the fuse or wind lighter. I will not enter here into the reasons why the iron match, as the pyrophoric lighter is called, is steadily replacing the ordinary wooden match, except to mention the safety connected with its non-poisonous nature and last but by no means least the great saving in bulk over the match, particularly in boat shipments. The great volume occupied by a comparatively small weight of matches is a serious problem, especially with the high cost of cargo space today.

The cerium alloy manufacture depends for its raw material upon the residues from the gas mantle industry. Formerly these residues were considered waste products, but today there are no surplus residues as the entire quantity produced is used in various other industries, as for example, the manufacture of flaming ores, special glass and pyrophoric alloys.

The first step in the preparation of ferrocerium is the preparation of the electrolyte. When it is considered that the raw material contains in varying quantities probably 15 or 20 different elements this is not such a simple matter. What is required is to get the special mixed chloride which is used as electrolyte free

[1] Manuscript received April 10, 1920.

[2] Consulting Chemical Engineer, New York City.

from substances which will subsequently interfere with the electrolysis; sulphur, phosphorus and silicon are particularly objectionable. The cerium electrolysis is the most difficult and peculiar electrolysis which I have ever seen or heard of. There are about eight different factors which must be kept in proper relation to one another, otherwise satisfactory results will not be obtained. It is therefore necessary to plot curves continuously during the run to make sure that conditions are the ones desired. If one of the factors is out of balance, it is not always possible to correct it, but from the curves it is always possible to predict the results, *i. e.*, what the approximate weight of the metal obtained during a unit of time will be.

The "cerium" or "misch," as we call it, consists of an alloy of the metals of the cerium group. They seem to form a sort of aggregate or nucleus so that the electrolyte can be entirely utilized. That is to say, there is no selective electrolysis whereby an impoverished electrolyte is produced unsuitable for further use. This does not occur if the electrolysis is properly carried out. The "misch" can be cast into molds. The metal is soft and tough, can be cut by a strong knife, and is not pyrophoric. It is similar in some properties to lead.

The "misch" is next melted and alloyed with iron to form the pyrophoric alloy. The regular alloy contains approximately 30 percent of iron. This alloy gives a spark. Other alloys, called special alloys, are made which give a flame, a shower of sparks, etc. The effect can be controlled by the composition of the alloy. Magnesium and zinc are used in the preparation of a special alloy. One of these special alloys is used for miners' lamps, where the flame effect instead of the spark is desired.

The pyrophoric effect depends upon the brittleness of the alloy and its low kindling point. The cerium group of metals is exceedingly active chemically, having a tremendous affinity for oxygen and nitrogen. The heat of oxidation is very great, being approximately the same as that of aluminum and magnesium. The "misch" metal melts about 650° C., or less. It has a density of 7. These three factors, great affinity for oxygen and nitrogen, low melting point, and high density, would recommend it as a scavenger and deoxidizer of molten metals, so we should expect it to

have unusual properties along this line, and it has. The great heat of combustion prolongs the fluidity of the melt and frees it of oxides, occluded gases, etc. I refer to a reprint from the *Iron Age* of January 29, 1920, a paper by Dr. Richard Moldenke, presented before the American Foundrymen's Association the latter part of last year. The author experimented with cast iron and obtained excellent results. The deoxidizing action was excellent, the castings were softer and more dense, feeding through the gates and risers was prolonged, and the formation of combined carbon retarded. The results showed greater machinability and soundness. Without cerium the transverse strength was 2090 lb. (950 kg.), and the deflection 0.11 in. (2.8 mm.). With 0.15 percent "misch" metal it was increased to transverse strength 2840 lb. (1290 kg.) and deflection 0.13 in. (3.3 mm.). The conclusion from this work is that the metal becomes softer, is machined more easily, is freed from gas and pin holes, is under less casting strains, and has less internal shrinkage than where the metal suffers from more or less oxidation through imperfect melting practice. The result of two foundry tests as given by Dr. Moldenke shows a uniformly good increase in strength, machinability, and soundness of castings, found as the result of cerium additions. The author found with additions of as much as 0.5 percent cerium none could be found in the castings. He concludes that the avidity of oxygen for cerium is so strong that after a portion has been used up on the molten metal, the balance must be oxidized by continued contact with the air over the ladle, showing cerium to be a particularly powerful deoxidizing agent, as other deoxidizers have this property limited up to a certain point, any excess remaining in the casting.

We have found cerium in the form of "misch" metal to be very useful for bronzes, monel metal and copper. It frees the metal from oxides, gases, and raises the tensile strength, elongation and reduction of area.

The following are some results with copper. Electrolytic copper melted under charcoal in a graphite crucible; cast in 1.5 in. (3.8 cm.) dia. x 12 in. (30 cm.), cast iron molds, with ⅜ in. (0.95 cm.) walls, (1) was poured first, then 0.25 percent cerium-copper (85–90 percent cerium) alloy added and (2) poured. The

respective ingots were machined to 0.505 in. (13 mm.) diameter standard tensile test specimens and pulled with the following results:

Tensile Strength (1)		
Elastic Limit	9,440 lb./sq. in.	(6.6 kg./sq. mm.)
Ultimate Strength	25,500 " "	(17.9 " ")
Elongation in 2 in. (5 cm.)	28.50	
Red. of Area, percent	23.60	

Tensile Strength (2)		
Elastic Limit	16,900 lb./ sq. in.	(11.8 kg./sq. cm.)
Ultimate Strength	26,740 " "	(18.7 " ")
Elongation in 2 in. (5 cm.)	33.50	
Red. of Area, percent	47.20	

DISCUSSION.

H. W. GILLETT[1]: This question of cerium in brass and bronze is one we should be a little careful about, particularly in using an excess, until more detailed information is available. I have seen some figures from a large valve manufacturing company who tried adding a rather larger amount of cerium than Mr. Hirsch has mentioned, and they found that the strength was not improved, but rather decreased, and that the percentage of "leakers" on check-runs, with and without cerium, was greater with cerium than without. The conclusion they came to was that the addition of cerium to valve metal, at least, in rather large amounts, had about the same effect as an excess of aluminum or silicon—very close to the action of silicon, so it would apparently be well to be cautious about using an overdose, if one is going to use it at all.

MR. FULLER: I would like to inquire to what extent the use of cerium increases the resistance of the copper, the electrical resistance?

ALCAN HIRSCH: In the experiments given here there was no cerium left in the copper and the electrical resistance was at least equal to that of the starting material, which was electrolytic copper. I would like to say, while I am on my feet, in answer to Dr. Gillett's statement, that he is correct in that cerium oxide has a

[1] U. S. Bureau of Mines, Ithaca, N. Y.

very high melting point and it is necessary to see that the proper slag or flux is used so as to remove the oxide from the melt and not leave it in, otherwise you would get a poor result. We have made experiments on iron showing that it is possible to get very soft and very pure iron in the center and then to have the cerium oxide in it and get a weak casting in that way, so it is most important that the oxide should be fluxed out. I would also like to say that this whole matter must not be taken too seriously.

E. O. BENJAMIN[2]: May I ask Dr. Hirsch if any attempts have been made to utilize pyrophoric alloys for automobile ignition in order to overcome the ignition trouble.

ALCAN HIRSCH: Eleven years ago I made such an invention with the help of the chief mechanic of the machine shop of the University of Wisconsin, and we made long rods of it. It ignited the gas very well, but unfortunately there is an oxide formed which has a very deleterious effect upon the cylinder walls, and the amount of metal that would be used in a 4-cylinder, 1,200 r.p.m. machine would be quite considerable. We probably would like it to go into commercial use, but I do not believe that it is feasible.

COLIN G. FINK[3]: I would like to ask Dr. Hirsch if in the electrolysis of his salts he has ever tried any anode besides a carbon anode?

ALCAN HIRSCH: Yes, we have tried a good many different anodes, but the only one that has worked successfully is graphite.

COLIN G. FINK: Did you ever get any metal with any anode other than graphite or carbon?

ALCAN HIRSCH: No, I never did.

[2] Chief Chemist and Engineer, International Oxygen Co., Newark, N. J.
[3] Head of Laboratories, Chile Exploration Co., New York City.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, C. Townley in the Chair.

ELECTRIC FURNACE POWER FROM THE STANDPOINT OF THE CENTRAL STATION.[1]

By E. A. Wilcox.[2]

ABSTRACT.

Running comment on various aspects of the relations of electric furnaces to the power station, such as comparison with other kinds of power station loads, methods of charging for power, off-peak service (particularly to steel castings plants), continuous *vs.* intermittent service, power rate schedules, power factor, load factor, single-phase service, two-phase service, three-phase service, different systems of furnaces and their demands on the power supply, output of small high-powered *vs.* large low-powered furnaces, brass furnaces, smelting furnaces, general desirability and growing importance of electric furnace loads. [J. W. R.]

One electric steel furnace with an annual production of 55 tons in use in the United States in 1908, whereas approximately 300 electric steel furnaces with an annual production of over 500,000 tons were in service in 1918—ten years later.

POWER REQUIRED.

Assuming the average energy required for melting and refining steel to be 600 K.W.H. per ton, it is found that over 300,000,000 K.W.H. was used for this purpose alone during 1918. At the beginning of the current year there were estimated to be approximately 900 electric steel furnaces in service in the world, with an annual production of 1,500,000 tons. By the same method of figuring it may be assumed that at least 900,000,000 K.W.H. of

[1] Manuscript received March 8, 1920.

[2] Vice-President, Pittsburgh Electric Furnace Corp., Pittsburgh.

energy is used annually for this purpose. At one cent per K.W.H. the revenue from steel furnace load alone would therefore amount to $9,000,000 annually. Although these are not actual figures, they serve to indicate the phenomenal growth in number of installations and the potential possibilities afforded power distributors for disposing of energy and building up profitable loads.

BUYERS SPECIFYING ELECTRIC STEEL.

By no process of imagination can it be assumed that the market is saturated. The field has barely been scratched. In addition to the natural growth of demand for high-grade steel castings, it is observed that foundrymen are rapidly coming to appreciate the advantages of the electric process over other methods, and that steel buyers are more and more frequently specifying electric steel in their orders. Where high-grade medium- and small-size steel castings are required, the electric steel cannot be excelled either in quality or cost of production.

COMPARISON WITH OTHER PROCESSES.

In the manufacture of tool steels, no other process can compete with the electric furnace. The crucible process, which was formerly used exclusively for making tool steels, is rapidly being supplemented or actually supplanted by the electric method. Crucible costs alone amount to more than the entire melting and refining cost of electric steel, and for the latter much cheaper melting stock may be used. No refining is possible in a crucible and only high-grade material may be charged, whereas the electric furnace makes it possible to refine less expensive material to any desired limit. In the manufacture of alloy steel and the finer grades of carbon steel, the electric furnace is rapidly replacing the open-hearth process.

The demand for electric furnaces in the metal industry may be said to be greatest in the steel-producing sections, second in the large industrial machine manufacturing centers, third in territory devoted to manufacture of brasses and non-ferrous metals, fourth in the malleable iron-producing sections, and fifth in the cast iron foundry districts. It is confidently predicted that the latter class may eventually become one of the largest users of electric furnace equipment, as the possibilities become more widely known.

WIDE APPLICATION OF ELECTRIC FURNACE.

Not only are the crucible, converter, and open-hearth processes being set aside for the electric, but in the realm of the cupola and air furnace the electric method is beginning to make inroads. It has been found that electrically melted cast iron, for instance, has from 50 to 90 percent greater strength than ordinary grey iron castings. Owing to the higher superheat attainable in the electric furnace, it is unnecessary to melt iron high in phosphorus in order to insure rapid running of the metal for making light, thin-section castings. The naturally high freezing temperature of white iron makes the superheat obtainable in the electric furnace very desirable for pouring malleable castings. Absence of slag and gas occlusions, as well as freedom from other impurities in electric cast and malleable irons, distinguishes them from those made by fuel processes. While this particular field of the electric furnace has hardly been touched, the possibilities for development are quite obvious. For the melting and refining of both steels and irons, the electric furnace has practically no limitations, especially where quality, strength and soundness are worthy of consideration.

HEAT TRANSFER EFFICIENCIES.

It is possible to obtain a heat efficiency of 60 to 80 percent in an electric furnace, whereas the heat transfer efficiency of the open-hearth varies from 8 to 12 percent, and the crucible furnace from 2 to 3 percent. With 14,000 B.T.U. coal costing $5.00 per ton and electricity (3,412 B.T.U. per K.W.H.) costing one cent per K.W.H. the relative number of B.T.U.s obtainable may be roughly calculated for average heat transfer efficiencies to be as follows:

Process	Average Efficiency Percent	B.T.U. for 1 Cent
Crucible	2½	1400
Open Hearth	10	5600
Electric	70	2400

These figures naturally do not take into consideration the heat generated due to chemical reactions within the furnace nor the

grade of coal required. It is well known, of course, that only special grades of fuel (low in sulphur) can be used in fuel-fired furnaces, whereas the cheapest grades of coal may be fired under a boiler for generating electric power. A modern turbo-generator will, in fact, product 1 K.W.H. of energy with a fuel consumption of 1½ pounds (1.36 kg.) of coal, or even less.

EXPLANATIONS NECESSARY.

Lack of understanding often exists in the relationship between central station companies and furnace users. Such misunderstanding is almost always due to ignorance of each other's viewpoints. Lack of understanding of this sort tends toward development of a Bolshevik attitude—upon the part of the user at least. It is, therefore, of the utmost importance that the furnace customer should be educated to understand the power company's rulings, rates, and conditions under which service is rendered, if mutually profitable and satisfactory relations are to be enjoyed.

I think that power distributors have two pronounced tendencies that work to their great disadvantage in dealing with furnace customers; one is to unnecessarily complicate their systems of doing business with the individual and the other is failure to explain fully the reasons for so doing, regardless of how well their policy may be justified. The average customer wants only the assurance that he is being dealt with fairly, and with such assurance he is likely to reciprocate, in a measure at least.

CENTRAL STATION RATES.

Some points over which discussion may easily arise and on account of which misapprehensions may come about, are here considered. The first difference of opinion will often come with a discussion of the rate question. It is the topic which to most users of power is shrouded in mystery. It is unfortunate that rate tariffs often appear far more complicated than their application actually proves them to be. It is true that very few if any companies intentionally complicate their systems of rates with the object of confusing their customers, although the opposite impression may be easily created in the customer's mind.

METHOD OF CHARGING.

Rate schedules are usually devised to cover two variable costs. The "demand" or "readiness-to-serve" charge is intended to cover interest, depreciation, and other overhead costs on that portion of the line, substation, and power plant required or set aside to handle the customer's load, and which might be put to other use were the customer disconnected from the lines. The "energy charge" is intended to cover operating costs, such as oil, fuel, labor and other running expenses. The demand charge is determined from the load connected either by suitable recording instruments or by reference to the rated capacity of the apparatus. The energy charge is determined monthly from a reading of the integrating or kilowatt-hour-meters installed on the customer's premises.

DEMAND CHARGE.

The usual methods of calculating the demand are as follows: The user may be charged a certain amount per kilowatt per month on the basis of the name-plate rating of the apparatus. A 500 K.W. installation, for example, might be charged $1.00 per K.W per month, or $500 per month in addition to the kilowatt-hour charge as recorded by the integrating watt-hour-meter. This so-called "demand charge" could justly be made whether or not any current was used by the customer during the month, and for as many months as the customer is connected to the power company's lines.

Some power companies base their demand charges on the "peak loads" as recorded by curve-drawing instruments. The "peak" is the maximum load (usually expressed in kilowatts) maintained over a specified period of time. It may be taken as anywhere from five minutes to one hour. The demand charge is then determined at the end of the month by averaging a certain number of the peaks occurring during the month and multiplying the result by the charge per kilowatt of demand. It is obviously to the company's advantage to measure each peak over as short an interval of time as possible and to compute the average from a small rather than a large number of peaks. The more progressive power companies are now basing their monthly demand charges for furnace loads on the average of the daily peaks of half-hour duration or greater. Where the rate per kilowatt of demand has not been

excessive, this method of charging has generally proved satisfactory to everyone concerned.

PEAK MEASUREMENT.

Provided the peak is integrated, it can well be measured over a period of thirty or sixty minutes. If this is done, the producer of energy may have a supplementary provision that the peak determined shall be no less than 30 or possibly 50 percent of the instantaneous peak. The demand charge for the month may then be determined by averaging an agreed number of the highest peaks occurring during the month. It is most often the practice to reset the peak each month. Where this is done, provision is sometimes made that the demand charge for any month shall not be less than half of any previous month. Often, however, when an average peak is determined for one month it is used to definitely establish the demand charge for a period of months or until there is some modification of the connected load.

EXPLANATION OF RATES.

Two characteristics of electric furnace loads that naturally entitle users to lower rates are the amount of energy required and the character of power that is supplied. Central station companies are, of course, able to supply wholesale power at rates much lower than retail power. A single furnace may consume more energy than several hundred retail customers and yet require no more attention or labor cost on the part of the power company than any one of its retail customers. Large generating units, transformers, power lines, protective devices, switchboards, and other electrical equipment installed for handling furnace loads also involve far less investment cost per unit of capacity than the equipment required for supplying small retail customers. Furthermore, the manufacturers of electric furnace apparatus frequently supply the entire sub-station equipment, including transformer, protective devices and switchboard apparatus with the furnace installation, so that the user may negotiate for his supply of power at the voltage of the power company's transmission line or generating station. This arrangement reduces the power company's unit investment cost far below that required to supply an equal load of retail power and lighting service.

RAW CURRENT.

A feature which further justifies the granting of lower rates to furnace users is that loads of this character do not require the close regulation which is always necessary on distribution circuits supplying retail power and lighting customers. Raw current, in fact, may be furnished from separate circuits without involving any cost to the power company for expensive regulating equipment. The modern practice of up-to-date power companies is to allow a discount of 5 percent on loads of this character when energy is taken at primary voltage.

OFF-PEAK SERVICE.

During certain "peak-load" hours of the day it is often desirable to keep heavy loads off the power circuits. Most companies supplying electric energy feel justified in quoting considerably lower rates to furnace customers who can and will agree not to use their equipment at such times. The period is frequently the two or three hours following sunset, and oftentimes the furnace user can readily arrange his schedule so as to shut down his furnace during this time.

When a customer agrees not to run during the peak-load periods of the distributing company it is often the practice to base the demand charge on a percentage, say 50 percent of the normal peak. The customer is in that way rewarded for the inconvenience he suffers on account of interrupted operations, and the power company can well afford the sacrifice in revenue to obtain benefit of the improved load condition.

OFF-PEAK SERVICE IN STEEL FOUNDRIES

Operation of furnaces during off-peak hours may be accomplished to advantage in many steel foundries. It is often difficult to secure good men, however, who will work efficiently setting up moulds during other than daylight hours. Where sufficient labor is available and moulding space permits, it is often possible to set up a sufficient number of moulds during the day to take care of metal melted during off-peak hours.

The difficulties encountered in moulding by day and casting by night apply more generally to small than to large casting work. Many large casting moulds require several hours or even days to

prepare and when finished they may as well be left over for the night shift to pour. Only a comparatively few moulds are set up for medium and heavy castings and the space they take up is relatively small. The floor area required and the difficulties attending the setting up of a large number of moulds for pouring small castings during off-peak hours often discourages such practice.

When producing ingots, for rolling mill use for instance, off-peak operation may have marked advantages. A comparatively small amount of labor is required for handling the moulds and such labor may be directed as well at night as during the day. It may therefore be said that metal for ingots as well as for medium and heavy castings can often be melted more economically during off-peak hours provided the power companies encourage such practice in devising their rate schedules.

ADVANTAGES OF OFF-PEAK SERVICE.

Co-operation of the power companies in working out possible off-peak schedules may frequently result to their own advantage, as well as to that of their customers. Off-peak power sold at low rates is often more profitable than regular power service. On the other hand, regular power rates may often prove burdensome to the customer while building up his business or when lack of market for his product forces him to operate intermittently or at reduced capacity. It is customary and quite logical to materially reduce the "demand" or "readiness-to-serve" charge when energy is sold on an off-peak basis.

CONTINUOUS VERSUS INTERMITTENT SERVICE.

Continuous operation is generally to be preferred to intermittent operation. It insures the central station a more uniform load and a more attractive load factor. It encourages lower rates to the customer and, as already stated, power rate schedules are usually devised to take care of this feature.

REDUCING POWER CONSUMPTION.

Assuming a three-ton acid furnace under continuous daily operation requires 550 K.W.H. per ton, it is often found that the first heat in the morning will require approximately 700 K.W.H. per

ton, the second heat 600 K.W.H. per ton, and the third heat normal consumption. These figures are based on good average practice where the furnace is charged hot, and the doors and glands luted tight to conserve the heat when it is shut down.

REDUCING REFRACTORY AND ELECTRODE LOSSES.

Intermittent operation also increases electrode and refractory costs. The first heat in the morning may consume 50 pounds of electrodes per ton, the second heat 25 pounds, whereas normal operation will average perhaps 18 to 20 pounds per ton. At the same time the refractory costs may be at least double the average figure, which may be taken as 40 cents per ton on a three-ton acid furnace.

ECONOMY OF CONTINUOUS OPERATION.

It is apparent, therefore, that continuous operation is most attractive to the central station and most economical for the furnace user. A small furnace operating continuously is more satisfactory than a large one operating intermittently. Of course, where large castings have to be poured, the furnace size must be sufficiently great to handle the largest of them. It is obvious from the above that heats in any case should follow one another as rapidly as possible, in order to secure the best and most economical results.

RATES NOT STANDARDIZED.

High demand charges are necessarily unfavorable for short-hour customers. Likewise high energy charges are objectionable to long-hour users. Although numerous attempts have been made to standardize methods of charge, little thus far has been accomplished. It may be assumed, however, that concerns distributing hydro-electric energy can better justify high demand and low energy rates, and conversely steam generated energy can more consistently be sold on the basis of low demand and proportionately higher energy rates. Present-day tariffs, however, are often anything but logical and seldom is attempt made to justify them in their detailed application or on grounds other than the total income which they create. For this reason the individual customer or class of customers may often be made to suffer or benefit, as the case may be.

OPERATING DATA.

The following tabular data show comparative outputs, energy consumption, billings and unit costs for making acid electric steel castings of medium size. It indicates the advantage of continuous operation as opposed to intermittent, from the standpoint of operating cost to the user as well as that of revenue to the central station company.

TABLE I.

Three-Ton High Powered Furnace Producing Acid Steel Castings.

Month	Tonnage	Total K.W.H.	Demand	K.W.H. per Ton	Month's Bill	Cost per K.W.H. in Cents	Cost of Power per Ton
1st	69	44,988	1000	652	$1577.89	3.51	$22.86
2nd	77	50,589	1000	657	1627.74	3.21	21.14
3rd	388	226,592	1000	584	2894.57	1.277	7.46
4th	614	341,384	1200	556	4055.51	1.188	6.60
5th	576	318,528	1200	553	3884.09	1.219	6.74
6th	1118	608,192	1200	544	6056.57	0.995	5.42
7th	907	488,873	1200	539	5161.68	1.055	5.69
8th	1456	762,944	1200	524	7217.21	0.946	4.96
9th	1284	677,952	1200	528	6579.77	0.97	5.13

The customers' bills were figured on the basis of the schedule of rates shown in Table II.

TABLE II.

(*a*) *Primary Charge*

Each month a primary charge is paid according to the following schedule:

First.....25 percent of maximum demand @ $4.00 per Kw.
Next.....25 percent of maximum demand @ 3.00 per Kw.
Next.....50 percent of maximum demand @ 2.00 per Kw.
Kw. in excess of maximum demand.....@ 1.00 per Kw.

(*b*) *Secondary Charge*

Each month a secondary charge in addition to primary charge is paid according to the following schedule:

First 50,000 Kw. H.....@$0.009 per Kw. H.
Next 50,000 Kw. H.....@$0.0085 per Kw. H.
Excess Kw. H.....@$0.0075 per Kw. H.

(*c*) *Discount*

From the secondary charge a discount of 0.005c. per Kw. H. is made on the first 100,000 Kw. H. for prompt payment.

The demand charge in Table II is somewhat higher and the energy charge is a trifle lower than is often available for this class of service. The energy is generated by steam, and while the average rate is quite fair, it is believed that the interest of both parties would be best served by lowering the demand charge and raising the energy charge. The rate is quite simple and easy to figure, however, and does not tend to confuse customers who are not accustomed to rate calculating. In this respect it is highly desirable.

Each individual central station company seems to have its own standard schedules of power rates. It is seldom that two of them are worded alike, but the majority of those in effect in this country are quite similar in their application. The "Wholesale Power Rate," shown in Table III, may be taken as a fair example of the make-up and kind of rate submitted to large electric furnace users. Such schedules are generally made a part of a formal printed contract.

TABLE III.

Available to customers with connected load of 200 kw. or greater.
Rate—

(1) Demand Charge:

For the first 200 kw.....	$1.50 per kw. per month
For the next 800 kw.....	1.00 per kw. per month
For excess over 1,000 kw.....	.75 per kw. per month

Plus—

(2) Energy Charge:

1.5 cents per kw. hour for first 10,000 kw. hours used per month.
1.0 cent per kw. hour for next 90,000 kw. hours used per month.
0.8 cent per kw. hour for next 200,000 kw. hours used per month.
0.6 cent per kw. hour for excess over 300,000 kw. hours used per month.

Maximum demand determined, at option of company, from the customer's connected load (total of name plate ratings) or by suitable instruments, same to be calculated by averaging the daily recorded maximum 30 minute peaks of the month. The succeeding 11 months billing to be based in these calculations unless the connected load is increased.

Minimum charge for any month, whether energy is used or not, to be no less than demand charge.

Deduction of 5 percent on demand charge when customer takes and measures current at power company's primary voltage.

Successive deduction of 5 percent on total bill for payment within 10 days from date of bill.

No discounts for use of "off-peak" power considered.

No deductions for maintenance of good power factor considered.

APPLICATION OF RATE.

The curves, Fig. 1, show the average rates that would apply under various conditions of furnace operation figured on the basis of Table III. For example, a furnace having a 1,000 kw. demand and operating at 40 percent load factor, would earn a rate of 1.15 cents per kw. hour. The same furnace operating at

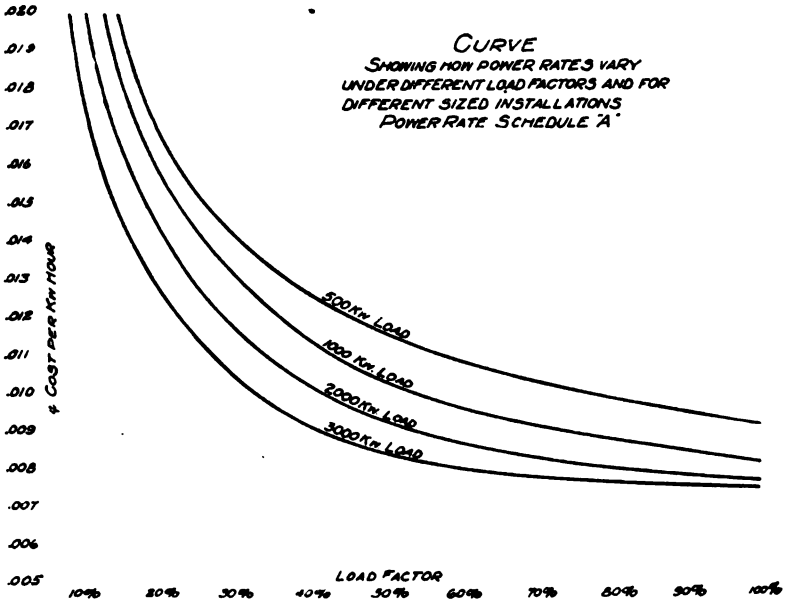

FIG. 1.

30 percent load factor would earn a rate of 1.33 cents per kw. hour. Under the same conditions of load factor operation, a furnace having 3,000 kw. demand, would earn rates of 0.92 and 1.06 cents respectively, and the relative output of steel in each case would be in favor of the larger furnace. The application of rate schedule A, as shown in Fig. 1, therefore demonstrates that the larger the furnace load and the greater number of hours it is used during the month, the lower the rate will become.

CONTINUOUS OPERATION EARNS LOWER RATE.

Another point brought out by reference to the curve is that a small furnace operating a large number of hours during a month may earn a far better rate than a large furnace operating fewer hours. For instance a furnace having a demand of 1,000 kw. and operating under 40 percent load factor would earn a rate of 1.15 cents per kw. hour, whereas a 2,000 kw. installation operating under a 20 percent load factor, would earn a rate of 1.47 cents per kw. hour. In other words, the advantage is with a small furnace operated to capacity, rather than with a large furnace operated intermittently.

POWER FACTOR.

The power factor of furnace loads is an important feature to consider. Some polyphase installations may have a power factor as high as 90 percent, single-phase long arc installations as low as 40 percent, and induction furnaces as low as 30 percent. Power factors below 50 or 60 percent are almost always considered undesirable additions to the power circuits, especially if they are unbalanced or single-phase loads. Ninety percent power factor, or greater, may on the other hand be too high for some individual operating conditions. Smaller power stations may favor power factors of 65 to 75 percent, whereas the larger ones may offer special inducements in the way of rate discounts for power factors maintained at 80 to 90 percent. Power factors may be varied somewhat by introducing reactance in the transformers, through increased magnetic leakage, or by the use of external reactance. The cushioning effect of such artificial reactance thus gained by power stations of limited generator capacity is sometimes considered advantageous even at the sacrifice of more desirable power factor conditions.

The curve, Fig. 2, shows the effect of different power factors, as determined by the amount of total reactance in the furnace, transformer, and line, on the maximum amounts of current obtainable under possible short-circuit conditions. It will be noted that very high current surges are possible on circuits designed for power factors above 90 percent.

CHARACTER OF LOAD.

Power companies, practically without exception, favor polyphase, rather than single-phase loads, where large heating, power, or furnace loads are concerned. The standard present-day practice is to generate and distribute electrical energy over three-phase circuits. The investment in power plant equipment and distributing lines is thereby largely reduced and polyphase power apparatus on the customer's premises is considerably less costly.

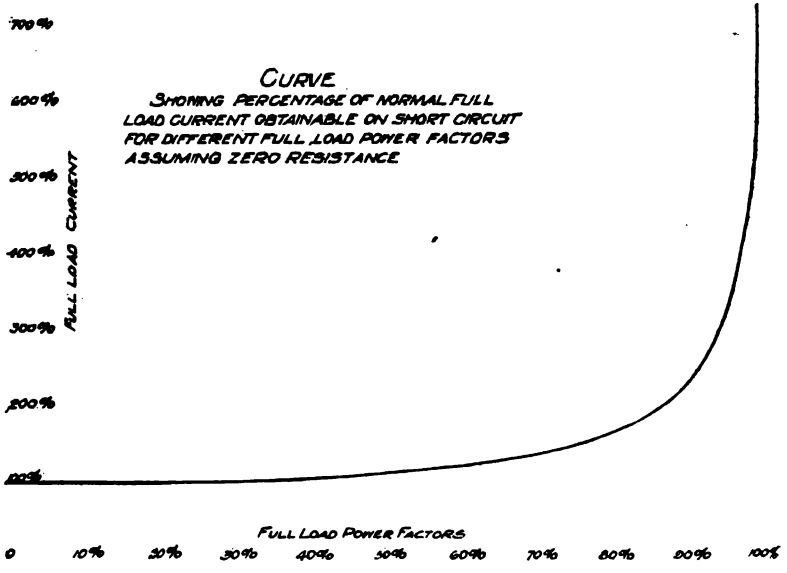

FIG. 2.

Some of the older companies, in isolated instances, yet employ two-phase power circuits, but these are rapidly being changed over to three-phase distribution.

SINGLE-PHASE SERVICE.

Of course, it is always possible to take single-phase current from polyphase lines, but immediately this is done, the other phases of the entire circuit, including the generating equipment at the power plant, become unbalanced; the load is not equally divided between the phases and serious impairment of the service and reduction of efficiency results.

TWO-PHASE SERVICE.

Two-phase current may be taken from a three-phase circuit or three-phase current from a two-phase circuit by means of the well-known "Scott connection" of the transformers. This arrangement results in considerable loss of energy and impairment of the efficiency of transformation and requires the use of transformers especially constructed for this purpose. It is quite apparent, therefore, that the use of three-phase equipment works to the mutual advantage of the parties concerned—namely, the central station company, and the furnace user.

INDIRECT ARC STEEL FURNACES.

The indirect arc has certain advantages for burning in furnace bottoms. This can be done without the use of broken pieces of electrodes as in the direct arc types. The operation has to be performed only once in each 500 to 1,000 heats, however, so the advantage is of no great importance.

The arc is naturally more steady and free from the fluctuations inherent to an arc in contact with cold metal. This feature makes it possible to operate at higher voltage and power factor and to require smaller secondary conductors but at considerable sacrifice of operating speed. Little saving is effected in electrode costs, however, because in practice their size is limited by their mechanical strength rather than by their current-carrying capacity.

LOSSES INCREASED.

Refractories are subject to much more intense heat with indirect than with direct arc furnaces. Even the smaller sizes require carborundum roofs to withstand the heat, but this material being an excellent conductor of heat is quite wasteful of energy. The white reflecting surface of the desulphurizing slag incident to basic operation, and this slag being a good heat insulator, is a distinct hindrance to successful basic refining. The heat is transmitted very slowly to the bath and reflects mostly to the roof and side walls.

BLOWING EFFECT.

The "blowing effect" of the indirect arc may be produced by two electrodes, three electrodes, or by two electrodes and a common return, provided in each case the conductors approach one

another at the proper angle. The blowing effect caused by the magnetic field set up is proportional to the square of the current flowing and tends to push the arc downward away from the electrode points. The counteracting effect of the heated air currents, however, tends to blow the arc upward and may easily overpower the downward magnetic influence, especially where a low current and long arc are employed. The mechanical design of most indirect arc steel furnaces with their large electrode openings and heat conducting roofs is such as to make them rather inefficient in operation and rather difficult to handle with automatic control.

ENERGY CONSUMPTION.

So many conditions enter into the subject of energy consumption per ton of steel produced that only rough estimates and comparisons with actual installations can be made. Smaller furnaces naturally are less efficient than larger ones. Furnace design from an electrical, mechanical, metallurgical and heat engineering standpoint has much more to do with the amount of current consumed than is often realized. Basic operation requires more energy than acid operation. A longer period of refining is required. The removal of the heavy slags before pouring permits the escape of heat in the slags and through the furnace doors. Acid furnaces on the other hand oftentimes require no slagging whatever.

VARIABLE OPERATING CONDITIONS.

The analysis, weight and form of the scrap or other material charged has a distinct bearing on energy consumption during the melting period. Heavy irregular pieces, for instance, melt more slowly, especially in a furnace that is not equipped for rapid operation. The longer the time taken for refining and making the necessary additions the greater will be the current requirements. Again, it is well known that when pouring very small or thin section castings the metal has to be much hotter than when pouring larger and heavier section castings. The superheating required for small thin castings therefore makes for higher current consumption.

It, of course, requires more time to turn out tool or alloy steels than to produce ordinary foundry castings on account of the longer period of refining necessary. Hence, the character and

analysis of the product has a marked effect on the electrical energy used. In addition to these points, it may be said that the number of hours of operation, the time between heats, the skill with which the refining is carried on and the necessary additions made, together with the ability and experience of the operator, has much to do with unit energy costs.

The data in Table IV show the operating results of a 3-ton acid furnace turning out medium-sized castings over a period of eight months at 24-hour operation. The costs are figured from Table III and are based on the first month's demand of 1,100 kw. To a central station man the rates per kilowatt-hour earned by the furnace user may seem very low. When he considers, however, that the furnace operation is continuous and observes the total monthly income, he will appreciate the valuable character of the load. The output of steel and the cost of power per ton of production should interest the steel maker.

TABLE IV.

Electric Energy Consumption and Costs on Rapid Three-Ton Foundry Furnace Making Acid Steel for Medium-Sized Castings. Twenty-four Hour Operation.

Month	K.W.H. Consumed	Monthly Billing	Average Cost per K.W.H. Cents	Tons of Steel Produced	Cost per Ton Steel
First	362,000	$4,049.15	1.118	603	$6.71
Second	524,000	4,754.75	0.907	904	5.29
Third	530,000	4,842.75	0.901	921	5.26
Fourth	613,000	5,362.05	0.875	1104	4.85
Fifth	650,000	5,572.95	0.856	1192	4.67
Sixth	555,000	5,031.45	0.907	991	5.06
Seventh	633,000	5,376.05	0.849	1151	4.67
Eighth	597,000	5,270.85	0.883	1076	4.90

DAILY OUTPUT.

In selecting a furnace it is highly important to consider daily output as well as tonnage (per heat) rating of the equipment. This is a matter that concerns the power company furnishing the energy, as well as the furnace user producing the refined metal. With electric furnaces of equal tonnage rating, one may be capable of turning out five, another ten, and yet another fifteen heats of refined steel of the same character in a 24-hour period.

FURNACE TRANSFORMERS.

From the power company's standpoint it may or may not be true that furnaces turning out the greater daily tonnage will produce higher demands on the power circuits. Seldom, if ever, does the demand increase in proportion to the furnace output and even though it did, the advantages far outweigh the disadvantages. Highly powered furnaces are generally sold complete with specially constructed furnace transformers having exceptionally strongly braced coils that are spaced to produce the proper cushioning effect. They are designed for a lower temperature rise under continuous operation and with a number of taps to permit wider variations of secondary or furnace voltage during the various operations. The latest designs are especially planned with the idea of producing a uniform, well-balanced power load. Only the novice in furnace construction will recommend the use of standard stock transformers for furnace work. It is true that the first cost of transformer and other electrical equipment may be greater, but the quick melting of the charge and subsequent rapid refining and superheating of the metal amply compensate for it. The assumption should not be made that any furnace may have its output augmented by simply increasing the transformer capacity, because such is not the case.

FURNACE DESIGN.

The furnace itself must be so constructed, from both mechanical and electrical standpoints, to handle the increased power and greater amount of heat without injury to the apparatus. In other words, furnace manufacturers must have a thorough knowledge of electrical and mechanical engineering, as well as of metallurgy, to produce the best and most efficient apparatus. Too often the development has been one-sided and has been the cause of many of the popular prejudices which yet exist. The heaviest power loads occur during the period of melting-down and it is obviously best to improve the efficiency as much as possible during this period.

ADVANTAGES OF RAPID OPERATION.

There are numerous advantages accruing to the furnace user from a more highly powered equipment. In the first place, his

investment cost may be reduced. A 1½-ton furnace of the more rapid design may do the work of a slower 3-ton furnace. It is well known that little or no refining of the charge takes place during the melting-down and the quicker this operation is performed the sooner actual refining may be begun and the required results accomplished. Likewise, rapid refining may be performed with greater precision, increased efficiency, and with less losses than slow refining. Furthermore, it is apparent that the quicker the superheating process is carried through, the less will be the losses and the sooner the metal may be poured into the moulds. With the heats coming frequently, less floor space is required for setting up the moulds. While the power cost of a furnace designed for rapid operation may be somewhat greater than that of a slower furnace, the user is concerned only with the cost of energy per ton of metal produced. If it costs him a dollar a ton less when produced in a rapid furnace, on account of his greater output, it is obviously to his direct advantage.

FURNACE POSSIBILITIES BECOMING RECOGNIZED.

The more progressive power companies are beginning to consider the electric furnace load from a broader angle and to base their schedules on the furnace load as a whole, rather than on the load of an individual installation. They realize the possibilities for growth of the furnace business and appreciate that its encouragement will result in the installation of a greater number of furnaces, better average load factors, and more attractive returns.

ELECTRIC BRASS FURNACES.

There are many uses to which the electric furnace is being put other than that of melting and refining iron and steel. There are estimated to be upwards of 200 electric brass melting furnaces in service. These are divided among the arc, induction and resistance types. The free burning indirect arc type naturally produces a more steady central station load than the direct arc customarily used in the steel furnace. The induction furnace of over 25 K.W. capacity, 60 cycles, or 60 K.W., 25 cycle, is of excessively low power factor, often 60 percent or less. It has to be operated more or less continuously, however, and when designed to eliminate

"pinch effect" the load is quite steady. The load of the resistance brass furnace may also be quite uniform where conditions are such as to make for continuous operation. It is estimated that the relative energy consumption of the arc, induction, and resistance furnaces of one-ton capacity, melting yellow brass would be 200, 225 and 350 K.W.H. respectively, under more or less continuous operation.

RESISTANCE FURNACES.

Much has been published regarding the wide application and use of resistance type furnaces for enameling, baking, vulcanizing, heat treating, tempering, and other purposes requiring temperatures of 1,600° F. (870° C.) or under. For higher heats the chrome-nickel wire or ribbon resistance is not very satisfactory on account of high maintenance cost. They may be used for treating steels of 0.40 percent carbon, or over, but are not well adapted for steels of lower carbon content. Resistance furnaces of this character are unusually attractive to central station companies, as they afford uniform, high power-factor, long-hour loads.

SMELTING FURNACES.

The demand for acetylene used in cutting and welding has revivified the carbide industry, and a number of new plants are now going in at points where good limestone and coke are available and where reasonably priced power can be obtained. Due to the continuous method of operation the carbide furnace load is an unusually attractive one. A large market for power for the operation of smelting furnaces already exists and is being rapidly extended for the production of ferro-silicon, ferro-chromium, ferro-tungsten, ferro-molybdenum, ferro-titanium, etc. Many central stations will be called upon to operate smelting furnaces, as the demand for alloy steels is extending rapidly. The load is naturally quite attractive, being similar in character to that of the carbide furnace.

FORECAST OF FURNACE POWER LOADS.

Electric furnaces are coming to be among the largest users of electric power. In fact, it is confidently predicted that they are destined as a class to become greater consumers of central station

energy than mining power installations and electric railroads. As compared to general industrial power loads, as well as exterior and interior lighting loads, the electric furnace will undoubtedly become a far more extensive user of power.

The loads created by electric furnaces of modern design are not unattractive as a class. They ordinarily operate over long hour periods and in the main insure good load factor and power factor conditions. Compared with many induction motor loads and with such apparatus as welders, rivet heaters, elevators and many other devices such as are used only during certain limited seasons of the year, or hours of the day, they are far more attractive to the central station. They usually take power in large blocks, at primary or high-tension voltage. They do not require the close regulation of line voltage that is so necessary for practically all classes of power and lighting loads, and once the connection is made to an electric furnace, relatively little operating expense is involved in providing the service.

The "direct" or "contact arc" maintains a higher power factor than ordinary induction motor loads, which never exceed 85 percent and often average 60 to 75 percent. It is also much more attractive than the irregular load of the small interurban or city street car system.

DISCUSSION.

E. O. BENJAMIN[1]: In the paper read by Mr. Wilcox particular stress was apparently laid on the advantages of the electric furnace to provide a balanced load for the power company, as well as for giving even power distribution. Also a comparison was made with power demand from public utility companies, such as for car service, but apparently no comparison was made with aqueous electrolytic demand. Electrolytic demand means a demand 365 or 366 days per year, 24 hours per day, in the production of oxygen, hydrogen, chlorine, sodium hydroxide and the refining of copper and numerous other metals. This is what we might consider our highest degree of utilizing power, the demand

[1] Chief Chem. and Eng., International Oxygen Co., Newark, N. J.

being constant 100 percent all the time. Out of 40 plants that I know of producing oxygen and hydrogen throughout the United States, 6 of them bring on their full load at off-peak periods. It would be interesting to compare an industry of that sort to the electric furnace to see its relative merits on the question of load distribution.

H. A. WINNE[2]: Two of the papers touch rather discouragingly on the possibilities of the electric furnace plant, having several furnaces, operating those furnaces on a schedule such that the load factor of the plant will be high. I realize that this is rather difficult to do, but I do know of one steel plant having some 4 or 5 furnaces, which is operating those furnaces on a schedule which gives a high load factor. They operate on a 6-day week schedule, starting off on Sunday night. One furnace is started up as soon as the men come to work, and the others at regular intervals thereafter so that there will be a furnace pouring every so often. The operators attempt to maintain this schedule throughout the week, and they have succeeded remarkably well; by bringing up the load factor they have reduced their power rate to such an extent that the saving in power cost much more than makes up for any additional cost in making the steel due to possibly holding a heat a little while to make it fit in with its place in the schedule.

As regards the possibility of limiting the peak load demand of a furnace plant, that is being taken care of in one or two installations that I know of by a device which will automatically cut off one or more furnaces, or reduce their power input, when the peak is reached. That device can be made to operate either on an instantaneous peak or on a combination of time and kw. peak, that is, on a kilowatt-hour basis, so to speak.

As regards the curve-drawing power-factor meter, after it is decided what the power-factor of an unbalanced load of the nature of an electric furnace load is, I hope we will have a power-factor meter that will graphically indicate that. At the present time we do not have such a device.

J. W. RICHARDS[3]: I will make some general remarks on the possibility of electrochemical processes filling up the valleys en-

[2] Elec. Engr., General Electric Co., Schenectady, N. Y.
[3] Prof. of Metallurgy, Lehigh University, Bethlehem, Pa.

tirely and making an even load factor for the power plant. At the present time many of our electrochemical processes entail expensive apparatus, and those who are using such wish to use them as nearly as possible at 100 percent load factor; but there are a number of electrochemical processes where the apparatus is not very expensive, where the power used might easily be made to fit into the valleys and perhaps reduced nearly to zero at the peak hours. For instance, in refining copper there is no harm done to the deposited copper at all by cutting down the current; you merely reduce the output. If a copper refinery were being run on a power-station line, its load could be reduced to almost zero at the peak times and run at full capacity in the valleys. The copper refiner does not want to do that because it cuts down his output. Frankly, the question is just a balancing of disadvantages and advantages: reduced output *versus* lower charges for power when smoothing out the curve of power-station load-factor. However, I think we ought to look forward to the possibility of electrochemists devising processes which will absorb large amounts of power from cheap apparatus which is capable of being run intermittently, just as intermittently for instance, as a storage battery, and under those conditions, with a cheap installation and a process which can be stopped and started whenever desired, I think one could look forward to using such an electrochemical process to absorb the whole of the valley of the load factor, which would enable the station to run at a steady load the whole 24 hours. The electrochemical plant would be, so to speak, floating on the line, so as to use for the electrochemical process whatever surplus power the plant had above the requirements of its other customers. The electrolytic production of oxygen and hydrogen is admirably adapted for such use.

F. G. DAWSON[4]: I would like to say a word about single-phase operation and power-factor as it affects the power plant and particularly the dynamos, from the point of view of the dynamo designer. The single-phase operation is just about the worst feature that could be introduced. Of course, if the load is small compared with the capacity of the generator, there is no harm done, but if that load is a large, single-phase load, there is bound to be a double frequency effect, not only on the field wiring of

[4] Installer and Gen. Furnace Advisor, Detroit Elec. Furnace Co., Detroit, Mich.

the dynamo but in the cases of the triple alternators and the metal retainers which are used to hold those field wirings against centrifugal stresses. The losses due to that double frequency action are enormous, and have been, in certain cases, so great as to melt out the metal wedges. Of course, wirings can be introduced which will reduce the liability to damaging the revolving field, but nevertheless there is still a big waste of energy and increased heating. I think it is a thing to be avoided just as much as possible. Now about power-factor, I feel it is not sufficiently appreciated. Almost all recent dynamos have the limit of their capacity in the revolving field, certainly a great many of them, and yet the duty put upon those revolving fields is largely due to magnetizing current, and obviously the higher the power-factor the greater output you can get out of that piece of apparatus. I had occasion not long ago to make a rough estimate of the possibilties of a certain dynamo, and I included the power-factor. It could be operated at 25 percent increase in kw. rating as compared with 80 percent power-factor, and the field still had a margin of 135, or 20 percent. That is to say that a 1250 kw. machine at 80 percent power-factor would carry 1500 kw. so far as the dynamo was concerned, with one-sixth less field-current than at the lower output and lower power-factor.

W. B. WALLIS[5] (*Communicated*): An electric furnace installation in the Pittsburgh district, consisting of two 6-ton units on alloy steel operation, has been regularly operated on load factor of from 75 to 80 percent. This is, of course, exceptionally good for steel-making furnace operation and has been accomplished by a cycle of operation such as suggested by Mr. Winne. In this same plant, due to the efforts of one man, the maximum 5-minute integrating peak was reduced approximately 30 percent. This was accomplished, first, by proper placing of the charge in the furnace; second, by use of lime during the melt-down period, and third, by proper handling of the furnace during that period when scrap is "shoved in."

We were able at another plant to reduce the 5-minute integrating demand from 2053 K.V.A. to 1455 K.V.A., without lengthening the time of heats.

There is one power company that has taken into consideration

[5] Pittsburgh Electric Furnace Corporation, Pittsburgh, Pa.

instantaneous surges, and has so fixed their rate that where the instantaneous demand exceeds by 50 per cent the 5-minute demand, one-half the difference between the 5-minute peak and the instantaneous peak is added to the 5-minute or billing demand. This makes it imperative that the furnace operator cut off power when shoving in his scrap, and neglect of this practice is costing a number of furnace operators in the particular district in question quite a sum of money each month.

The question of load factors which can be obtained on electric furnace installations is controlled, first, by the personal element in furnace operation, and second, by the design of the furnace installation.

The use of the electric furnace had very rapid expansion during the war-time period and admirably took care of the requirements of special steels in demand at that time.

It is only natural that in a rapid expansion of this kind certain phases of furnace practice were neglected. Of necessity, the metallurgical problems were given primary consideration. The result has been that some rather unfortunate records have been made as to power demand and load factors. This phase of the question is, of necessity, being looked into with respect to the lowering of prices, and the range of economies to be effected is indicated by figures given in the foregoing.

There is one other point in connection with the load factors on furnaces, namely that of the charging time required. I have in mind one 3-ton furnace installation where it regularly requires from 45 to 75 minutes to charge 8,000 pounds (3,600 kg.) of scrap, as compared to another installation where it requires twelve minutes to charge 9,000 pounds (4,100 kg.) of scrap, both plants charging by hand, the scrap being light scrap. Naturally, the latter plant has a much better chance to establish a good load factor.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, C. Townley in the Chair.

THE ELECTRIC-ARC MELTING FURNACE AND THE CENTRAL STATION ELECTRIC COMPANY.[1]

By Augustus C. Smith.[2]

Abstract.

A consideration of the effect the arc electric melting furnace has on the power supply, particularly of the surges on the line because of careless handling of the furnace during the melting-down period. Details are given of the abnormal requirements of a number of furnaces, and some, showing that they can be avoided by careful working. The author concludes that unless the furnace men are trained to handle the furnaces carefully during the melting-down period, the use in such furnaces on power companies' supply systems must be limited, because of the abnormal momentary peak currents. [J. W. R.]

At the beginning of the war there were comparatively few electric-arc melting furnaces operating from central station power. Owing to the tremendous demand for high-grade steel during the war period, the number of these furnaces was very materially increased and yet the number of arc furnaces operated from central station power is still very small, that is, the amount of electric energy diverted to this purpose is a relatively insignificant amount or the number of arc furnaces operating today, compared with what is to be expected in the future, is still small. It is, therefore, to the future demands from this class of service that the central station engineer should direct his attention.

The total of all arc furnaces now operating are widely distributed throughout the entire country, and even in localities where

[1]Manuscript received March 25, 1920.

[2] Buffalo General Electric Company.

several furnaces may be in operation, these furnaces are more or less scattered. relatively speaking, over the distribution system of the central station company supplying the service.

The future of the arc melting furnace is by no means limited to the steel foundry, but by degrees will find its way into the grey iron, malleable iron, and brass foundries, and for certain specific purposes into the larger steel rolling mills.

Up to the present time the operation of arc furnaces from the central station distributing systems has not caused any very serious disturbance to these systems, but as the number of furnace installations multiply and they become more densely located, the cumulative effects will become more noticeable.

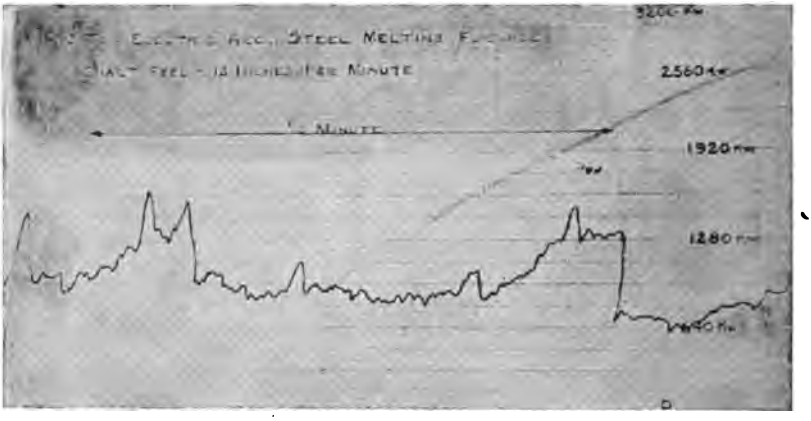

FIG. 1.

The power requirements of the arc furnace, varying instantaneously from zero demand to a short circuit, are more severe than any load the central station has been called upon to supply, and unless curbed in some manner may seriously retard the future development of this most promising field of electrical application.

This might be exemplified by a certain installation in a steel foundry in Buffalo, operating a 3-ton, 3-phase furnace. The electric service is delivered at 11,000 volts to three 333 kv. a. transformers located in the furnace transformer room. The transmission line supplying this service is not used for any other purpose, and the automatic oil switch at the power company's sub-station

end is set to open up at 320 amperes, the equivalent of about 6,000 kv. a. It is a common occurrence for this switch to open up several times during every heat on the furnace.

If there were ten, or even five similarly operated furnace installations on this sub-station, which is not a future improbability in this particular section of the city, the power company would not be able to meet their combined demands and some of the furnaces would have to be denied service.

If such a condition is a future possibility, the central station must immediately fortify itself against it. Their only means is to discourage this class of service, the alternative is moderation in furnace operation. The severe manner in which electric energy

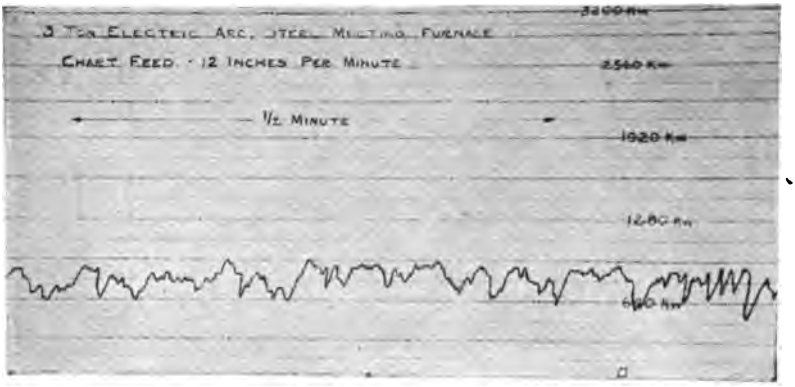

FIG. 2.

is used in the above furnace is not due to furnace design, but is caused by the method of operation. An identical furnace installation in another steel foundry never exceeds a momentary maximum demand of more than 2,000 kv. a. and usually much less.

Another very gratifying installation consists of two 10-ton three-phase furnaces where the combined momentary maximum demand of the two furnaces rarely exceeds 6,000 kv. a. The feeder switch controlling this circuit is set for 640 amperes, or the equivalent of about 12,000 kv. a., and very rarely opens up. These furnaces are assisted in keeping down excessive demands by the use of external reactance which is used only during the melting-down period.

The first steel-meiting arc furnace to be installed in Buffalo and operated from central station power was made in March, 1914. This was a two-ton single-phase hand-control furnace; the electrical energy furnished was 3-phase, 2200 volts, 25 cycle, transformed to 220 volts through two 750 kv. a. Scott-connected transformers. Current limiting reactance was permanently installed between the transformers and the furnace, which limited the current flow to three and one-half times normal. While about 800 kilowatts was the maximum power required at the furnace, 1500 kv. a. capacity was required on the primary of the transformers.

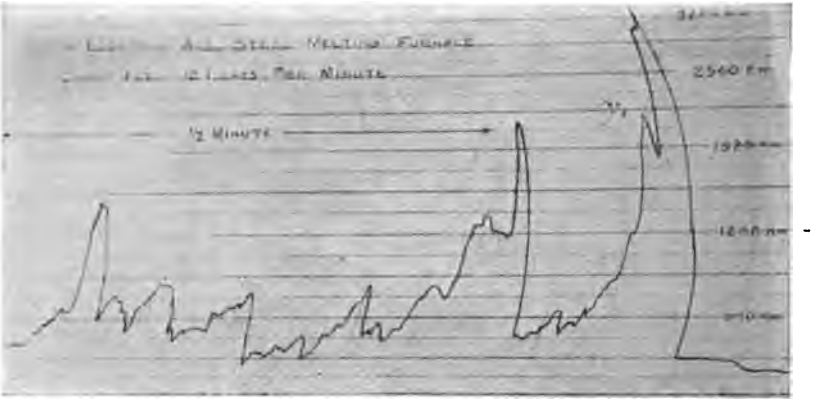

FIG. 3.

Following this initial installation, a second furnace, similar in every respect to the first furnace and with like amount of reactance, was installed, a third 750 kv. a. transformer was added, and the three transformers connected closed-delta on the primary. It was expected to obtain a better balancing of load across the three primary phases by the operation of the two furnaces, but this did not prove out, as the same power requirements in the two furnaces seldom occurred simultaneously.

These furnaces are still in operation, but on account of the low power-factor and phase unbalancing they are limited to the use of power at night only.

We have here four distinct furnace installations, the first two identical in equipment and free from any external reactance, the

third provided with removable 15 percent external reactance, and the fourth with 30 percent permanent external reactance.

In the operation of these different furnaces, the first of the two without reactance uses about six times normal current rating during the melting-down period, while the second rarely, if ever, exceeds twice normal current rating. It is quite apparent then that the method employed in furnace operation has considerable to do with the energy requirements of the furnace.

In the third installation the reactance is so connected that it can be cut in on the primaries of the transformers at any time during the heat by means of an oil switch. It is not customary,

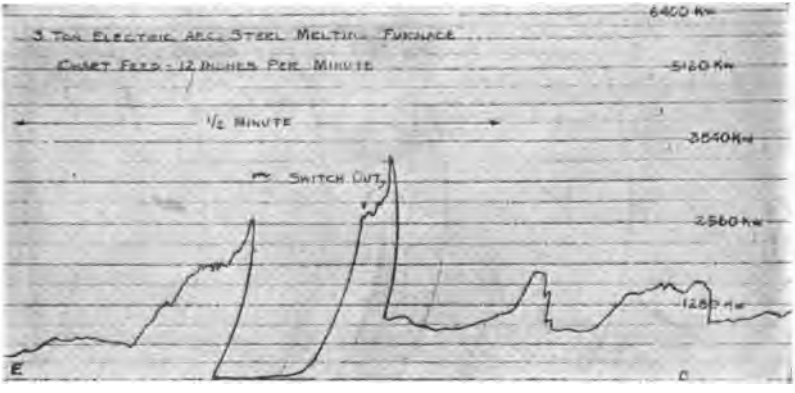

FIG. 4.

however, to use this reactance until the heat has been on for about a half hour, or when the electrodes begin to form a hole in the charge. When this reactance is put in use the voltage is increased about 10 percent by a change in transformer taps.

The external reactance and, possibly, the higher voltage used during the melting-down period in this furnace installation undoubtedly is of material help in keeping down electrical surges, but is not alone sufficient to entirely prevent excessive use of electric energy, and the reason that these furnaces seldom exceed their normal current rating is due to the operator's knowledge of both furnace operation and the electrical equipment used with the furnace and the skilled manner in which the equipment as a whole is handled.

The fourth furnace is ideal in its simplicity and comparatively free from very severe electrical surges but on account of its low power-factor and phase unbalancing is not acceptable to the central station as a day load.

The greatest difficulties which the central station is going to have from this class of service will come from furnaces which are improperly operated due largely to incompetency of the operator in charge and total disregard of the strain put upon the power company's system.

Unless something is done to improve these conditions of furnace operation, the central stations in the future will be compelled to impose penalties which will automatically prevent such reckless use of electrical energy and they may even be obliged to reserve

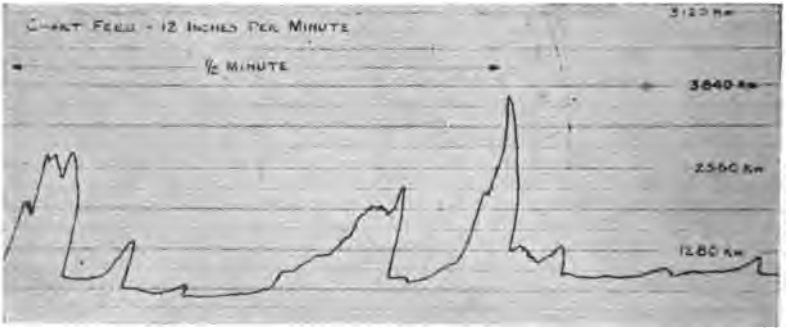

FIG. 5.

the right to discontinue entirely service to any furnace where the reckless use of electrical energy is persisted in.

Such a course if necessarily enacted by the central station would have a very marked tendency in many instances to discourage the adoption of the electric furnace.

It is, therefore, strongly recommended that, until such a time as the electric furnace becomes more generally used, and qualified operators more plentiful, that the electric furnace manufacturer should undertake the training of men for this work.

Particular attention should be paid to instructing a new operator how to properly charge his furnace, as the more severe electrical surges which occur during the melting-down period are frequently caused from the way a furnace has been charged.

He should also be informed as to the functions of the various electrical devices forming a part of the furnace equipment, their relations to each other, and instructed in their care, maintenance, and proper adjustment.

It is also suggested that a wiring diagram be furnished with every furnace installation. This would assist the operator in keeping informed of the various electrical connections and would be invaluable to the central station engineer if called upon for assistance in time of electrical trouble.

The general design of the arc furnace has been pretty well worked out. There is, however, opportunity for refinement of the electrical equipment.

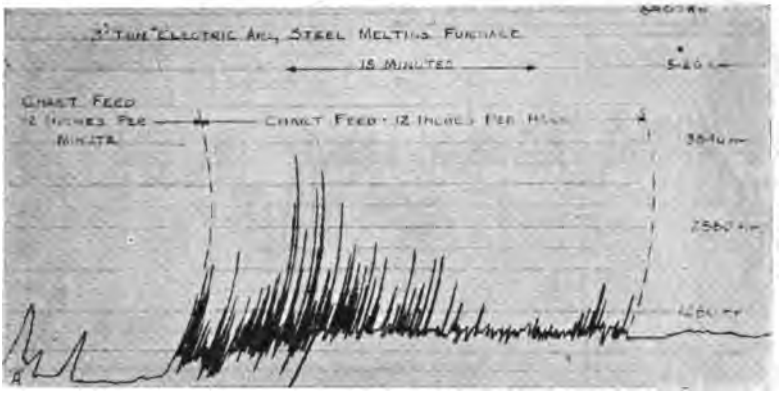

FIG. 6.

It is believed that furnace transformers should be provided with three or four additional voltage taps, each tap connected with a switch so that the voltage at the electrode can be changed any time during the heat.

It is also believed that a small amount of external reactance, possibly ten to fifteen percent, should be furnished and connected across a short-circuiting switch so that it can be put in or out of circuit any time during the heat.

Something more than the present electrical data available on furnace operation should be obtained before prescribing a standard for these transformer taps, and the same might be said as to the amount of external reactance to be used.

From some observations, crudely made, the indications are that a slight change only in arc voltage materially affects the furnace operation.

The common type of switchboard indicating meter and the ordinary commercial form of graphic recording meter are not suitable for obtaining essential electrical data on arc furnace operation, so that more or less special instruments are necessary for this purpose.

It is here that the central station company can probably be of greatest help to the furnace manufacturer by providing the instruments and conducting the necessary tests.

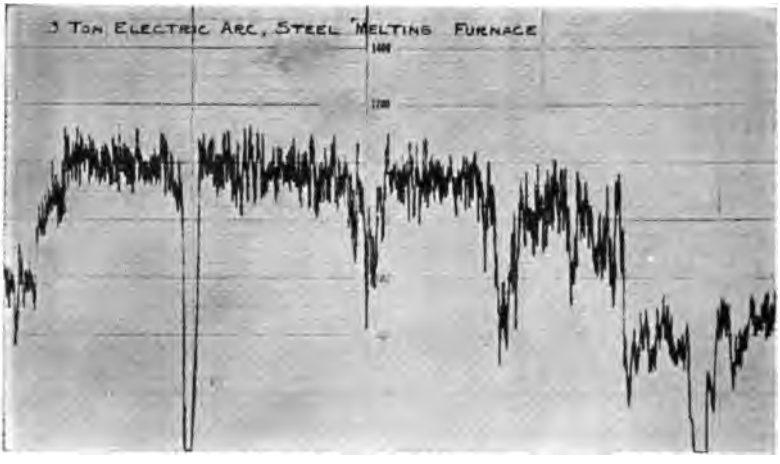

Fig. 7.

Some very interesting as well as instructive load diagrams have recently been obtained by tests made on arc furnaces with an Esterline graphic meter. The recording pen of the instrument used in these tests was capable of traveling the full scale in four-fifths (4/5) of a second and the chart feed was set to twelve inches per minute, so that a very accurate graphic record of the characteristic use of electrical energy by these furnaces was secured.

Photographic copies of these graphic charts are shown herewith, also a copy of the chart from the permanent graphic meter used to record this load.

With the prevailing high cost of foundry materials, the electric furnace becomes a formidable rival in productive costs with present methods of foundry practice; this, coupled with recognized superiority of product, justifies the expectancy of the electric furnace as a constantly increasing factor in foundry production.

As the central station company will be called upon to furnish the greater part of the electrical energy used in the operation of electric furnaces they become a factor to be regarded, and the electric furnace manufacturer should give more consideration to the problems with which the central station company is confronted.

With the co-operation of the electric furnace manufacturer along these lines and their assistance in regulating the operation of electric furnaces, it is believed that the central station company will be able to meet the future demands from this class of service.

DISCUSSION.

MR. COHEN: I have had considerable experience in the building of reactors and transformers with inherent reactors, and I feel from what experience I have had, that a great deal of good can be obtained by the use of automatic reactors which will prevent the high surges in current and demands on the power station.

E. L. CROSBY[1]: I believe we are fortunate in having with us a representative of the power company which probably has a greater number of furnaces and a larger melting furnace load than any other central station in the country. I would be glad if Mr. Noyes, of the Detroit Edison Company, would give us a few remarks on the way furnaces should be connected and tied into the system.

J. D. NOYES[2]: The Detroit Edison Company has never found it necessary to restrict the use of electric furnaces on its lines; you cannot handicap this business by fussy restrictions. All of our electric furnaces, both non-ferrous and steel furnaces, are served through distributing stations which have, or seem to have, ample capacity behind them to deliver the power required without

[1] Vice-Pres. and Gen. Mgr., Detroit Electric Furnace Co., Detroit, Mich.
[2] Sales Engineer, Detroit Edison Co., Detroit, Mich.

causing any trouble to other customers. Our general plan of distribution is from our central generating plants to sub-stations scattered over the whole industrial territory. These sub-stations are fed from 23,000-volt cables, and from the sub-station the outgoing power feeders and power transformers are entirely separate from the lighting lines and transformers, so that there is little or no interference between the fluctuating power load and the lighting loads. In general our steel furnaces are carried on separate cables from the sub-station to the furnace on the customer's property. The feeder cables are about the proper capacity to take care of the average steel furnace. We have some three-ton and some six-ton steel furnaces in use. We do not attempt to connect the electric furnace to the general distributing network. In regard to the brass furnaces, the load involved there is not of sufficient size to in any way cause difficulty of voltage regulation on the power system.

A. C. SMITH (*Communicated*): It has not as yet been necessary for the Buffalo General Electric Company to restrict in any way the use of electric furnaces. In supplying this service separate feeders are run from the company's sub-stations to the various electric furnace installations and our other customers have had no interference in their service due to furnace operations.

There is nothing intricate in providing for this class of service. However, as the electric furnace load becomes more densely located electrical disturbances can be expected from reckless furnace operation or improper design and installation of furnace electrical equipment.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, C. Townley in the Chair.

POWER PROBLEMS FROM THE STAND-POINT OF THE FURNACE OPERATOR.[1]

By WALLACE G. BERLIN.[2]

ABSTRACT.

A practical discussion of the nature of the power requirements when melting cold charges in the steel furnace. Different parts of the heat require differing amount of power, and produce different degrees of fluctuations of current. The effect of these on the power bill is considered, dividing the latter into "demand" power and "metered" power. The economics of running a large furnace slowly or a small furnace intensely is considered from these standpoints; also the question of running two furnaces in parallel so as to reduce the "demand" power, and of using off-peak power. [J. W. R.]

During the past year there has been a marked increase in the number of electric furnace installations. This increase is not only due to the high grade of steel produced by the electric furnace and now demanded by the steel market, but also to the fact that under many conditions of operation as met today the electric furnace can compete commercially in the production of small castings with converters as well as with the crucible process. Electric furnaces, when properly operated, produce a grade of steel which will readily replace crucible steel, thus eliminating the older and more expensive process.

The more progressive power companies are now studying electric furnace demands in a broader and more thorough manner than heretofore. In the course of this study they find it more

[1] Manuscript received March 3, 1920.

[2] Electric Furnace Operator, Taylor-Wharton Iron & Steel Co., High Bridge, N. J.

desirable to meet the general operating conditions of electric furnaces, rather than the special conditions of individual installations, as in the past. They find it desirable to encourage the use of electric furnaces, as it largely improves their average load factors and therefore their earnings.

One of the principal factors in the economical production of steel in the electric furnace is low consumption of reliable and cheap power. Actual cost of power is not to be considered at the expense of continuous service, and absolutely reliable continuous supply of power is the first requisite of cheap power.

The following observations explain this point. A furnace was operating under an average load of 800 kw.; a breakdown in the power house resulted in the stopping of one generator supplying the furnace, which made it necessary to reduce the furnace load to 500 kw. This condition continued for one hour. During the hour the melting advanced slowly, if at all, and increased the time of the heat and also the power consumption.

Another furnace was connected to the lines of a central station having no reserve equipment; the power failed when the charge in the furnace was melted, but not hot enough to pour into molds. The furnace operator held the heat in the furnace, and asked the central station the probable length of suspension of power, but received no satisfaction. The result was that the heat froze in the furnace. On receiving power the following day the solid mass had to be remelted, an operation requiring double the time and energy necessary to melt the original charge. During this remelting the hearth was cut to such an extent that patches had to be burned in before operations could be resumed. Interruptions of power became so frequent, with results as above, that the furnace had to be abandoned. The losses sustained under such conditions are measured not only in the cost of the additional power consumed, the labor wasted or the damage to the furnace, but what is more important, in decrease of the furnace tonnage output, which controls the price of all steel produced.

With a reliable power supply the factors which control low power consumption are:

(1) High load factor, or continuous operation, which results in large tonnage output.

(2) Strong, energetic furnace men, with good common sense, who can act in emergencies.

(3) Proper selection of scrap, which should be small and clean. Large scrap requires more time to melt down, and clean scrap helps to eliminate oxidation.

In selecting an electric furnace it is equally important to consider the daily output as well as the rated capacity of the furnace. Furnaces of the same rated capacity have a very unequal daily tonnage, depending on the number of heats possible. This variation in the number of heats depends upon the process used; for instance, a furnace operating on the basic process may be capable of producing 6 heats in 24-hour continuous operation, while the same furnace when operated on the acid process may produce 10 heats on continuous operation, an increase of two-thirds.

The furnace practice in the basic process consists of patching the banks with dolomite as soon as the heat is poured out of the furnace; the next charge is then introduced, which consists of heavy melting scrap. The electrodes are then lowered and the current turned on at the full capacity of the transformers. In about 30 minutes a pool of molten metal is formed under each electrode; during this period the power fluctuates heavily. Lime is then added and the power input settles down to a steady value, except small fluctuations due to the scrap falling on the electrodes. In about 1¾ hours the charge is melted, a sample withdrawn and the carbon determined by analysis or fracture. The bath is then "ored down" or "pigged up" until the proper composition is reached. The slag is then drawn off and a new slag made, of lime and fluor spar. After coking over with ground coke the desulphurizing and deoxidizing start, and in 20 minutes a white slag is formed which completely deoxidizes the steel in about 30 minutes. Alloy additions are then made and the heat brought up to pouring temperature.

In melting manganese steel scrap the same practice as above is followed, except that only one slag is used. More trouble is encountered in starting a heat, due to the poor contact of the scrap caused by the coating of rust on all manganese scrap. A higher voltage is advantageous to overcome this resistance and in every case it is necessary to start a heat by making contact with iron

rods and working the scrap until the arc will continue without assistance. This difficulty will increase the time of a heat from 2½ to 3½ hours. During the melting down period the current fluctuations are heavy and of momentary duration, causing unbalanced phase conditions.

A furnace load with these characteristics should necessarily be connected to a central station capable of turning out large blocks of energy; otherwise the heavy surges caused by the poor contact and intermittent arcs would produce poor voltage regulation, which would be fatal to the peace and happiness of the central station unless the furnace load was a small proportion of the total load connected to the power lines. The central station and the furnace operator have to consider from different standpoints in deciding whether the investment in an electric furnace or the investment in the power plant and transmission lines should or should not be made. From the operator's standpoint the decision depends on the market for his product, the amount of power the furnace will demand, and the existence of a power supply of a reliable nature. The central station is compelled to consider all its investments as permanent or distributed over a long period, and to charge back the expense contingent on the service. Hence the smaller power companies cannot, and the less progressive will not equip themselves to handle the new furnace loads without charging excessive rates; for they have to take account of the impossibility of selling their capacity to some other industry in case the furnace is abandoned. Since the electric furnace can compete in production with the other processes, there is no reason to anticipate an installation shutting down as long as the required reliable supply of power is furnished to the furnace.

Another point in power supply is that due to fixing of rates by the public service commissions and regulations affecting distribution, the small and unprogressive stations are protected from the invasion of the more progressive central stations. The following will illustrate: A power station of limited capacity undertook to supply a medium-sized furnace. The result was very irregular service, which limited the furnace output to a very small percentage of its possible capacity. The load factor was very small, with resulting large power consumption and excessive charge per KWH. Within a few miles of this plant a power company was

operating with a sufficient capacity and reserve to supply this furnace with a steady supply of power at the same rates. If the operators had been able to buy their power from this larger plant, they would have been able to secure steady power, increase their output and decrease the power consumption so that their power costs per ton of metal would have been reduced by half and the furnace installation would have been successful instead of a burden to the operator. In the steel castings trade there appears to be no reason why the electric furnace which has been developed to a high degree should not largely supplant other processes. Close co-operation between the furnace operator and the central station can develop this position quickly, but it will be necessary for the smaller power companies to do their part as well as the more progressive stations, to help make the electric furnace a permanent success.

Rate Schedules.

Rate schedules are based on two main charges, namely, a "Demand," or "Ready-to-serve" charge, which covers overhead charges, interest and depreciation of the power plant, substation and transmission lines supplying the customer's load. This is a just charge, made as long as the load is connected to the power lines whether any current is used or not, as this equipment cannot be used to supply other loads. The second is the "Energy charge," which covers the running expenses, fuel, attendance, etc. This charge varies according to the hours that the load is used as recorded by integrating wattmeters, while the demand charge is usually determined from printometers or special registering demand meters.

These rate schedules are presented in printed form and seem very complicated to the consumer. It is not necessary for the furnace operator to be confused, for if he will state his operating conditions, the power engineer will figure the rate and explain it very quickly. The most essential factor to the furnace operator is the cost of power per ton of steel produced.

The central station can supply the large consumer at lower rates than those quoted to the retail trade, because the cost of service and the investment for the equipment necessary to supply the large consumer is less per unit than to the smaller consumers.

The character of the current supply is also considered in the rate making, since the regulation of the power supplying the electric furnace is not necessarily as close as is required by industrial power and lighting loads.

There is no occasion for serious consideration of power factor at the present time, as a well designed furnace if properly installed will operate at a power factor of 0.80 to 0.90 during the early stages of the melting period and as high as 0.95 during the refining stage. The high current surges can be taken care of by the use of artificial reactance.

The following wholesale power rate may be taken as a fair example of the average make-up of rates submitted to the large power consumer.

Wholesale Power Rate.

Available to customers with a connected load of 200 kw. or larger:

Rate:

(1) Demand charge.
For the first 200 kw., $1.50 per kw. per month.
For the next 800 kw., $1.00 per kw. per month.
For excess over 1,000 kw., 75 cents per kw. per month.

Plus:

(2) Energy charge.
1.5 cents per kwh. for the first 10,000 kwh. used per month.
1.0 cent per kwh. for the next 90,000 kwh. used per month.
0.8 cent per kwh. for the next 200,000 kwh. used per month.
0.6 cent per kwh. for excess over 300,000 kwh. used per month.

Maximum demand determined, at option of company, from the customer's connected load (total of name plate ratings) or by suitable instruments—same to be calculated by averaging the daily recorded maximum 30 minute peaks of the month. The succeeding 11 months' billing to be based on these calculations, unless the connected load is increased.

Minimum charge for any month whether energy is used or not, to be no less than the demand charge.

Deduction of 5% on the demand charge when the customer takes and measures current at power company's primary voltage.

Successive deduction of 5% on the total bill for payment within 10 days from date of bill.

No discounts for use of off-peak power considered.

No deductions for maintenance of good power factor considered.

These curves show the average rates that would apply under various conditions of furnace operation on the above rate sched-

ule. For example, a 3-ton furnace operating on a demand of 1,000 kw. and a load factor of 20 percent, (which would be the operating conditions running single shift and turning out 3 heats a day), would earn a rate of 1.6 cents per kwh. The same furnace operating on a 24-hour schedule, or a load factor of say 45 percent, would earn a rate of 1.1 cents per kwh. Where the power consumption per ton of steel would be 700 kwh. the saving in power alone would amount to $3.85 per ton of metal. Under

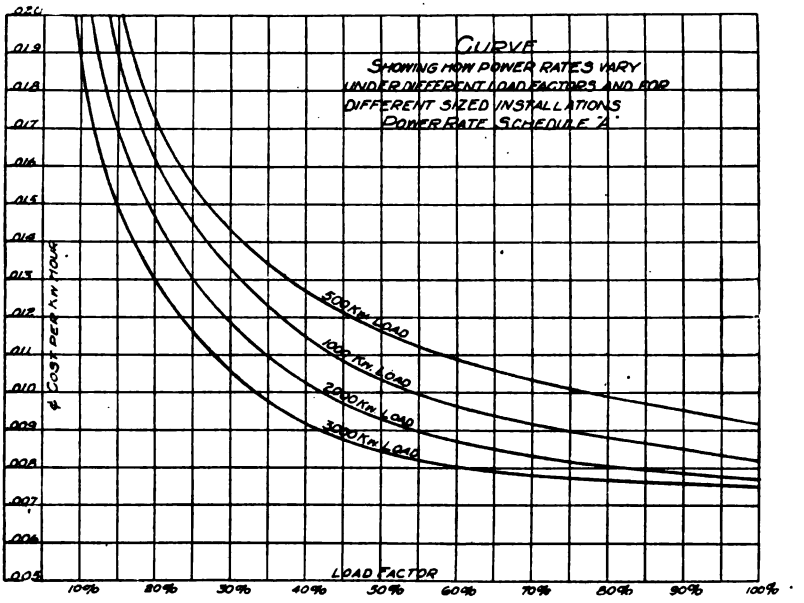

FIG. 1.

the same conditions, a furnace with a demand of 3,000 kw. and operating on a load factor of 20 percent would earn a rate of 1.35 cents per kwh., and if operating with a 45 percent load factor the rate would be 0.9 cent per kwh. This shows that the larger furnace using the larger block of energy, even with the higher demand, will earn a rate, which if considered alone would favor the larger furnace installation; also that the smaller furnace operating a larger number of hours will earn a rate far better than a larger furnace operated only a few hours. For example a 3-ton furnace operating at 1,000 kw. demand and having a 45 percent

load factor would earn a rate of 1.1 cents per kwh., while a larger furnace with a demand of 2,000 kw. and on a 20 percent load factor would only earn a rate of 1.47 cents per kwh. The advantage, of course, is with the smaller furnace operating at full capacity, rather than with the large furnace at half capacity.

Parallel Operation.

Parallel operation of two or more electric furnaces taking power from a single power station is economical where there is an ample and reliable power supply, provided they are run to capacity, and bearing in mind that the rate per kwh. depends on the load factor more than on the demand. If two furnaces are operated on the same line it is not probable the demand would be doubled, since the fluctuations may not occur at the same time. In furnace practice the heavy fluctuations occur on the melting-down period, and if the furnaces were operated to avoid these fluctuations occurring at the same time it would mean that the charge in the first furnace would have to be completely melted before the other furnace was started up. For example, take a 3-ton furnace running on a schedule of a heat every 3 hours, of which 2 hours is spent in melting and 1 hour in refining and charging. The capacity of the furnace would be 8 heats or 24 tons per day. The second furnace would be started 2 hours later than the first and its charge would only be half melted when No. 1 furnace would be ready to start again. Thereby a delay of 1 hour would be necessary, which would mean that a heat would be poured from each furnace every 4 hours, thereby reducing the capacity per furnace to 6 heats per day or a daily output of 18 tons. The result in the demand would be a reduction of about, say, 500 kw.; or the total demand would be 1,500 instead of 2,000 kw. with a loss in production of 6 tons of metal per furnace or a total of 12 tons per day. The effect of this restricted operation would be to lower the load factor from 45 percent to 35 percent and reduce the demand from 2,000 kw. to 1,500 kw.; the curve shows that this would result in an increase in the rate from 1 cent to 1.2 cents or 0.2 cent per kwh. With a power consumption of 700 kwh. per ton of steel this increase in restricted operation would amount to $1.40 per ton of metal produced, without considering the loss of 12 tons output of metal per day.

A further advantage of unrestricted operation is that if larger heats are needed for heavy work two furnaces can be poured at the same time without the necessity of a larger capacity furnace. In many cases a larger furnace is a disadvantage, as to pour the large heat into small work takes a lot of time and requires a large moulding space.

Off-Peak Power.

There are hours of the day during which it is highly desirable to keep certain heavy loads off the power circuits. The usual period or periods is at the start of the industrial day and two or three hours after sunset, depending on the character of the industrial load. Most companies supplying power are willing to quote lower rates to furnace operators who will agree not to use power at such times. The concessions vary in different localities; when power is supplied from a small station it is sometimes advisable to arrange the schedule of operations to use off-peak loads and take advantage of the concessions, since the power is likely to be cut off at times of heavy load anyway, and the schedule might as well anticipate this.

From the operator's standpoint it would be more economical to run the furnace on a full schedule, thus keeping the load factor high and reducing the losses of heat, which means more efficient operation. It is important that the furnace should be operated with the shortest possible periods between heats, for during such periods the operator loses a portion of his demand time, which increases the ready-to-serve charge. Also the furnace lining is cooling down quite rapidly and the electrodes are oxidizing away more rapidly than when melting a charge. In some cases the off-peak rates are available at prices which do not comprise more than a portion, if any, of the demand charge. In such cases it is more economical to operate the furnace during the off-peak periods, as nights, holidays, etc.

Isolated Plant.

The writer is operating a furnace of 3-ton capacity Heroult type, which receives its supply from an individual generating unit. The equipment installed to meet the requirements is as follows:

One 600 hp. Springfield water tube boiler. A water tube boiler

was selected due to its being able to handle the fluctuations and heavy overloads.

One 1,250 kw. Allis-Chalmers Parsons steam turbine, high speed, condensing, with a safety stop to regulate the speed in connection with the governor. The overload valve admits steam to the low pressure blades, thus taking care of sudden fluctuations and overloads.

The generator is the two-pole revolving field type, 3,600 rpm., 60 cycle, 3 phase, 2,300 volts, feeding three 500 kw. transformers situated above and directly behind the furnace.

The turbo-generator was selected because of its lower first cost per unit, high efficiency, very close speed regulation, and economy at all loads. Its enormous overload capacity and the rapidity with which it takes up the fluctuations are probably its most important advantages.

The troubles encountered were few considering the small installation and lack of reserve capacity. Regulation was poor and the unit could not be synchronized with the rest of the plant load. When trouble occurred with the other plant equipment it was necessary to shut the furnace down to keep the plant supplied with power. On one occasion oil worked into the boilers and caused them to "foam," which made their operation very uncertain, and at times when the fluctuations were frequent the water was drawn over into the turbine, which might have proved disastrous. In such an installation, too, there is always the possibility of the furnace generating equipment burning out, which would cause a long delay in furnace operations until repairs could be made.

DISCUSSION.

CARL HERING[1]: Mr. Berlin referred to the advantages of making furnaces smaller and running them at higher speed, that is, forcing them; it was therefore of interest to me to recall the fact that it was only a few years ago that I offered a paper to this Society pointing out the advantages of using smaller furnaces operated more quickly. At that time this was a heresy, and

[1] Consulting Electrical Engineer, Philadelphia, Pa.

the paper was refused by the committee, but nevertheless was quickly accepted for publication elsewhere. Now it seems that my recommendation was right. What was a heresy a few years ago is now accepted as good practice; this shows that we are progressing. My argument was that the most efficient form of electrical furnace is the electric fuse, which burns out when there is an excessive current. The thermal efficiency of that little furnace is very nearly 100 percent, for the simple reason that the operation is completed before any heat can get lost. A fuse is not what we would call a furnace, but in fact it is one and it teaches us a good lesson, which is that if we have to deal with high temperatures, the sooner we get through with the operation the better; because just as long as the high temperature is kept up, so long will there be heat losses. Therefore it seems to me that to run a smaller furnace with a smaller charge, but force it as much as possible and get through the period of high temperature as quickly as possible, will be saving considerable heat losses. It is therefore in my opinion, better, when other conditions permit it, to run smaller furnaces at high speed rather than larger ones at slow speed.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, C. Townley in the Chair.

THE ELECTRIC FURNACE AND THE CENTRAL STATION.[1]

By H. L. Hess.[2]

In referring in any way to the central power station as affecting the electric steel producer, I do so with some hesitancy as my connection is, and always has been, primarily with the power user. The subject is, however, of vital importance at present and bids fair to become increasingly so as new and possibly larger melting units are installed.

It is not very many years ago that the electric furnace was a new and untried proposition, and in figuring on the load probabilities, the central station man of necessity formed his estimate of the desirability, or lack of desirability, of the load, upon more or less theoretical information and usually with very little regard to working conditions that might exist in actual plant operation.

Today, unless the furnace is of a radically new type, many successful installations and much data collected by electrical equipment manufacturers and furnace builders, enable a definite forecast as to the probable load to be worked out, based on concrete examples.

I recall the great indignation aroused among the population of one rather small town where we operated some earlier types of furnaces, when our wildly fluctuating load shut down the moving picture houses. Naturally, the industry of lesser importance suffered and the moving picture houses went serenely on.

Many unfortunate experiences in the past have been mainly due to extremely heavy fluctuations in the use of current and the unbalancing effect upon the distribution system. Some installations were made on small power companies' lines, and the effect of the heavy fluctuation was disastrous both to the steel and power companies. The new designs of 3-phase arc furnaces and proper

[1] Manuscript received February 7, 1920.

[2] The Hess Steel Corporation, Baltimore, Md.

regulating control equipment go a long way towards preventing any serious difficulties, provided the power system is of sufficient capacity to absorb the fluctuations without any injurious consequences.

Today there are in excess of 300 electric steel melting furnaces in the United States alone. "The Iron Age" of January of this year gives the number as 323. The increase in number in 1919 was not as great as that of the war years of 1917 or 1918, but this is natural, as during those years every effort was being made to increase production in our endeavor to end the war. Thirty-six installations were made during the last year; January, 1919, there were 287; January, 1918, 233; January, 1917, 136, and back in 1913 only 19, and these largely of experimental and anything but successful types.

The electric steel produced in the world in 1918 is estimated at 1,155,273 tons, with the United States in the lead, with 511,364 gross tons, or approximately 50 percent of the total. This is, I believe you will admit, a very creditable showing for a new industry facing the natural prejudices of a buying public educated through years of usage to the older types of crucible, open hearth and Bessemer steels. It has not all been clear sailing, and the electric furnace, unlike Topsy, did not just happen to grow, but developed in proportion to its ability to demonstrate outstanding advantages and a product of superior quality.

The universal experience in most branches of industry, is that the earlier experimental and development work is carried on by the individual industries themselves, and that the designs and equipment worked out, due to lack of specific knowledge, are often crude. As soon, however, as a demand for a certain type of equipment is developed and the use shows signs of stabilization, the manufacturing concerns specializing on equipment of allied nature, join in the work and are able to work through the intricacies and difficulties and solve many originally perplexing problems.

Development of the latest type of electrical furnaces, and subsidiary equipment for these, and the enormous strides in the adaptation of electricity for heavy mill drives, are examples of this, and show what can be done when the trained experience of experts is brought to bear upon a subject. Broadly speaking, a desirable electric load for a power company, is one that gives to

the power company a revenue which justifies all expenses of supplying this electric load. In the same manner, an undesirable load is one that does not return the required revenue to the power company, and therefore handicaps it in supplying good service, not only to that particular load, but also to its other customers.

The expense to the power company of supplying a given service is divided into two general cost items, namely, fixed and operating. The fixed cost consists of various items, the principal of which are interest, amortization, taxes, and insurance on general plant fully equipped, distribution system, buildings, etc. The operating cost consists of items such as labor, fuel, and all items of expense not included in the fixed cost. A desirable load from the power producer's point of view is one that fully pays its proportion of these fixed charges, or one that permits of lower operating cost during a 24-hour period because of absorption of overhead charges during off-peak periods.

Naturally, in order to compete successfully in his business, the power user must get his power at the lowest possible cost consistent with uninterrupted service and entire dependability of supply. There must also be a feeling of confidence in the ability of the central station to furnish at all times sufficient current to keep pace with the development of a still growing industry.

Basic differences of operation in the steel mill and central station cause differences of ideas as to the billing for power, and it is decidedly difficult to get together on a mutually satisfactory basis. The central station must install generating capacity of ample size to produce sufficient power to meet the maximum contracted for requirements of its customers, and the expense of this equipment, even though partially idle at times, must be absorbed in the charges made and billed the customer. This is the justification for the demand charge. Reduced to a bare fact, it means that should the power demands contracted for by all customers be added together, the KW. obtained would equal the generating capacity of the company. I believe many power companies upon analysis would be found to have insufficiently large installations to meet this obligation.

This billing can be done in many ways. Each customer in full operation builds up a demand upon the generating equipment that must be taken care of even though this full requirement is only

drawn upon for a limited number of hours per day, or week. Based upon past schedules and cost experience, the central station figures out a billing method which consists, for instance, of a charge (usually a sliding scale charge) for the KW. of demand established, and supplements this with a charge for the KW.H. actually consumed. Usually, too, there is a definite allowance of a certain number of KW.H. for each KW. of demand, a rebate being given for the KW.H.'s not consumed under this allowance; or, if the allowance is exceeded, a sub-charge is made. It is in my experience unusual, if not impossible, for steel melting plants with their power ratio, to use the full allowance customarily given by the power company and obtain the minimum KW.H. charge.

This method of billing is entirely fair, but it imposes certain hardships on the user, as the steel business, particularly that division making only a limited range of grades, is notoriously affected by general trade conditions. Formerly it was said that the industry was either a "prince or pauper." Things are probably better today, but the demand for steel still varies widely and rapidly.

To produce to full capacity, all units are put into operation, a demand is set up which often holds from then on to the expiration of the contract, as per contract agreement, but although the demand is high and the charge proportionate, it is perfectly satisfactory, for the steel output is also large and the cost of power easily absorbable. When, however, dull times come along, and the power required is comparatively small, the high demand charges as already set up, must still be absorbed by the smaller output. Instead of being able to produce steel more cheaply all the way through, in order to compete favorably, the sales price is penalized by the higher charges for an unused article—current; and so, although entirely fair and a logical method of billing from many points of view, this feature of power consumption remains somewhat of a bugbear to the furnace operator.

An advantageous method for the consumer is that used by at least one power company. Here a new demand is established for each interval of six months. This permits increase in equipment on both sides and does not impose a long term of undue hardship on either party, be the times good or bad.

Another way for the central station to take care of its charges, if the elimination of the demand feature is desired, is to make the

charges directly on the K.W.H. consumed, with sometimes a minimum consumption charge, in which case, however, this charge has the same effect as a low demand charge during periods of minimum operation. On the other hand, if any such provision is made by the power company, to safeguard against periodic load demands, the straight KW.H. charge must be high enough to absorb average variations, and again the customer is up against an economical stone wall.

This system of a definite charge for KW.H. of power consumed has, however, many advantages, and it should be possible in many cases, where a close relationship and understanding of the working conditions exist between the central station and the electric furnace operator, for them to work out a schedule that permits the balancing of peak-loads of the power company by plant load control, with a saving to both, due to uniform operation, which saving should be shared as a rate reduction to the large power consumer. This is being done to some extent in some localities, and may work out to advantage as time develops the industry. In the meantime you cannot get something for nothing, and the balancing of the load and the selection of the best equipment and control appliances are of primary importance, as affecting the desirability of the load for the central station and of economy of operation for the user.

The individual power plant built and operated by the electric steel manufacturer can only be considered in unusual cases, as the installation of such a plant runs into very large expenditures, and can only be afforded by large concerns. With such installations, one of the greatest weaknesses of central plant service is eliminated as the transmission lines necessary are comparatively short. A large amount of the central station's trouble in supplying a customer, seems to be in transmission line failure. Reliability of operation is of prime importance, and this factor should be studied very carefully before putting up a metallurgical plant that will be entirely dependent upon the central station for its supply of power.

Where both steam and water power are used by the central plant, power produced by means of steam is often supplementary to the water power, the steam units acting as a reserve during periods of low water in summer or freezing in winter. A com-

bination of this kind, if well balanced, insures the power user a continuous supply, with little likelihood of a complete shutdown, and should insure a low power cost. In most industries, the cost of power to the total cost of product manufactured, may be considered as 5 percent or less. In the electric steel industry, however, this ratio is considerably higher, and a low rate is of prime importance.

The power factor of a furnace or group of furnaces enters into the question of economy of operation, as it is the ratio between the apparent power and the useful power. In other words, apparent power in a 3-phase system is volts $\times$ amperes $\times$ the square root of 3, and this only equals the actual power when the power factor is unity. Actual power in a 3-phase circuit is volts $\times$ amperes $\times$ the square root of 3 $\times$ the power factor expressed as a percentage. As a rule the KW.H. meters register only actual power, and the customer is billed for this.

As a low power factor makes it necessary for the central station to carry equipment or capacity to generate the apparent power as shown by the volt and ampere meters on their boards, to overcome this wattless or lost energy due to the customer's poor power factor conditions, there is more and more leaning towards the installation of graphic meters which indicate the power factor. This is a subject of very great interest and has a decided bearing on the possible economy of furnace operation.

In melting down a charge in an electric furnace, the current fluctuations are comparatively great. The degree of fluctuation varies to some extent with the type of material being melted, but more with the type of furnace and particularly with the electrical and control apparatus. It is naturally desired to melt down as fast as possible, as tonnage output during this stage of steel manufacture plays an important part in the costs.

One of the arguments against the feasibility of the electric furnace for the manufacture of quality steels has been the possibility of burning the steel due to the intense temperature of the arc and the alleged possibility of the transference of this high temperature locally to the small points of contact in the material being melted. Although it is possible to ruin a heat through bringing it up to a uniform temperature above that which is metallurgically correct, there seems to be no evidence to back up

the contention that this burning of the product during melting down is necessary or even possible. On the other hand, there are thousands of tons of remarkably good steel to back up the belief that no such condition exists.

There is, however, a limit to the amount of current that should be fed into the furnace which is not dependent upon electrical possibilities, but upon the economical balance between the tonnage produced through quick melting and the cost of furnace upkeep and furnace lining and repairs. It is possible to burn out linings and roofs completely in a few heats if care is not used, particularly if the furnace is not designed to take care of the maximum limit of power input.

During finish melting and refining, a much lesser amount of heat is needed. In fact, during certain periods of refining, it may even be advantageous to cut out the power entirely, and between heats, and while charging, bottom patching, etc., no power is, of course, used. This being the case, it is seen that an unequal consumption of power is the rule rather than the exception.

It might be supposed that with multiple units, a smoothing out of peaks could be effected. To some extent this may be the case, but heats in a furnace rarely follow any prescribed rule, and it is not possible so to regulate furnaces that the melting down and high demand charges dovetail in with the lower demand incidental to the refining or charging periods of other furnaces in the same battery. Holding a heat in order to regulate the demand is not only expensive through the delays incurred, but as the metallurgical balance between molten steel and slags is constantly changing, this necessitates extreme care with the increased possibility for off-heats.

This variation in power requirement may be called the load factor of the plant, or the ratio of the average power to the maximum power during a certain period. It is this load factor, as it of necessity must be in electric furnace melting plants, that makes a contract containing a definite demand charge onerous during dull times, particularly when, as just mentioned, this demand once established holds for a long period of years. The demand factor expresses this, as it is the ratio of the maximum demand to the total connected or established load of the system.

Often through carelessness an unusual peak is permitted to

run through the period required to establish a new demand figure. Such penalization of the customer, when spread through monthly charges over a period of years, runs into large aggregate sums. To check this, some type of signal device that will flash a series of colored lights, or sound a gong, when say 10 percent below the established demand and again when the demand is reached, is of assistance, but no entirely satisfactory method has as yet been worked out, as not only the maximum instantaneous demand must be taken into account, but the time element factor used in the establishment of the demand.

Many designs of electric furnace have been worked out, and naturally some of these have been more successful than others. I was formerly connected with a firm that I believe was among the first to see the advantages and possibilities of electric furnace steel, and although our first furnaces were not particularly successful, the experience we gained was most valuable.

As we were at that time operating a crucible steel plant, our inclination was toward the application of electric heat to crucible melting, and our first work was with a small Helberger crucible furnace. We later ourselves built several models of larger and differing types of crucible furnaces, but found great difficulty in obtaining crucibles that would stand up under the intense heat. There seemed to be always a weak spot due to a variation in the composition of the pot that would melt out, permitting molten metal to run into the bottom of the melting chamber, causing many complications and much difficulty.

We later operated a small one-ton Stassano furnace connected to a 3-phase circuit with manually operated electrode control. We were able to obtain fairly satisfactory steel from this furnace, but due to the effect of the arc, there was a tendency towards the forcing of the slags back from the center and hotter portion of the bath to the cooler outer surface of the molten metal. This decreased the dephosphorizing, and particularly the desulphurizing action of these slags to a marked extent, and made the removal of sulphur an uncertain and difficult matter.

For commercial operation on a moderate or large scale, the furnace adopted should not only be capable of absolute control. but it should be rugged and it should, if possible, be of a type widely used. It is then more easily possible to obtain workmen

familiar with this furnace who know at least the rudiments of operation. This is a decidedly important factor when the melting organization is of considerable size, due to the multiplication of melting units. This uniformity of type also permits economy in the carrying of spare parts, and makes it possible to shift furnace crews with very little revision of operating practice.

Modern electric furnaces are of the arc, resistance, and induction types, or a combination of these; certain points of advantage apply in a general way to most of them.

Electricity as a source of heat not only permits of rapid melting at a rate determinable at will, but it is the only absolutely clean and uncontaminated heating agent. Its one drawback as a metallurgical fuel is its high cost.

It is conceded, I believe, that until the advent of electrical furnaces, the crucible method of steel production for quality and tool steels was pre-eminent. The size of the crucible charge is limited to approximately 100 pounds, and the product of each crucible varies. Uniformity of analysis is difficult to obtain, and the method is costly. It would seem, then, that that method of steel melting that most nearly approximates crucible practice and crucible conditions, is the practice that will give best results, particularly if the disadvantages of the furnace and metallurgical factors are to some extent eliminated.

The electric furnace correctly operated is a large crucible heated by pure heat from within rather than a contaminated heat from without, with all the added advantages of positive heat control, and, to a large extent, atmospheric control as well—in other words, a highly perfected tool in the hands of a metallurgist or experienced operator.

It is a common statement that the electric furnace permits the use of cheap raw materials. It is true that the electric furnace for certain types of work, such as castings, etc., is capable of melting a low-priced grade of raw material and of producing a steel of higher grade than that produced by other competitive methods in the same type of business. Where, however, the product desired is of high quality, such as is required for the better grades of tool steel, it is advisable to use raw materials of the best character obtainable. It is due to this care, or lack of care in the

selection of base metals, that the wide variation in the price of electric steel is often confusing to the purchaser.

The crucible furnace can only melt the materials charged into the pot, as no refining is possible. There is a slight change in analysis from that theoretically calculated from the raw materials due to contamination by the elements entering into the manufacture of the crucible, and it is here that the electric furnace operating on carefully selected materials leads, as the furnace hearth may be considered as a large crucible in which heat containing no impurities is applied in an atmosphere that can be very carefully regulated. Great care is naturally required, as the melting and manufacture of quality steel cannot be reduced to an exact science, but requires experience obtained only through long practice, and is an art requiring careful thought and study, and a thorough study of the principles involved.

Exaggerated claims by electric furnace manufacturers have, and still do, lead to many disappointments. The method has in some cases been looked upon as a cure-all for the troubles, natural and otherwise, inherent in the manufacture of steel of any kind. As a result, some decidedly poor steel has been put upon the market, masquerading under a name deserving of a better backing. Recently a customer of a certain steel company rejected several carloads of electric steel with the statement that it was not 3½ percent nickel steel but 2½ percent dirt and 1 percent mud. It will take some time to convince that man that the material he bought was not typical of electrical furnace steel.

Open hearth electric steel, which consists of metal taken from the open hearth furnace and charged hot into an electric furnace for further refining, fills a decided want, if steel superior in quality to open hearth steel and at a price consistent with competitive requirements is required, but steel made in this way does not compare with the higher grades of cold melt electric steel or crucible steel. The characteristics of open hearth steel remain in the final product even though refined in an electric furnace, unless this refining is carried to an extent not economically feasible.

In melting in the open hearth furnace the source of heat or flame carries with it certain impurities which contaminate the metallic bath and give off elements, such as sulphur, that are difficult of removal. It is difficult to obtain and control a neutral

flame in the open hearth furnace, and such control means a loss of calorific power. As a result, the iron, carbon, silicon and manganese of the bath, are absorbing the oxygen and other gases which are only partially removable from the steel by the addition of deoxidizing agents. Dead melting is difficult, if not impossible.

There is very little possibility of disagreeing with the necessity for as nearly neutral an atmosphere during melting as possible. How long would a crucible melter hold his job, if he were to remove the covers from his pots and expose his carefully calculated charge to the ill effects and contamination of the furnace gases? The only commercial limitation to the heat it is possible to obtain from the electric arc is the ability of the furnace refractories and furnace construction to stand up successfully.

Alternating current is used for steel melting almost exclusively because of the possible chemical action and induced electrical current effects following the thermal application of direct current power, and its disassociating effect upon the constituents of a molten bath. There is also the difficulty of controlling the carbon of the steel due to the anode to cathode action between the carbon or graphite electrodes, which action also affects the slags used for refining.

Alternating current is furnished within a wide range of voltages to local transformers, either as single, two, or three-phase, and customarily as 60- or 25-cycle. More modern central stations almost universally generate three-phase current, although local conditions may in certain cases decide in favor of two-phase, or even single-phase, and there are certain requirements necessitating the furnishing of direct current power.

The prevalence of three-phase systems to a large extent has influenced the furnace builders in their designs of furnaces; most of these are constructed for three-phase operation. A two-phase furnace can be connected to a three-phase system, as this can be transformed to two-phase by means of suitable transformers Scott-connected. A single-phase furnace connected to a single leg of a polyphase system, is undesirable, as it puts a heavy unequal load upon the generating equipment, the seriousness of this depending upon the size of the single-phase load as compared with the total load on the generator. Any further peak on one of these phases, due to the fluctuating load of the furnace

operation, is felt far more than the same variation spread over a three-phase furnace load.

Sometimes rotary transformers are used, a three-phase motor driving as a single-phase generator, but this increases the furnace installation cost, which overhead must be carried and added to the operating costs. Low frequency means higher cost of generating equipment, but within limits is advantageous for the furnace operator, as the power factor falls as the frequency rises.

There are certain outstanding differences in the type of electrical equipment used for electric furnace operation, but regarding these we cannot go into detail. One difference is in the transformers. In some installations of three-phase furnaces, three individual transformers per furnace are used, and, in others, a single three-phase transformer. There is undoubtedly economy in the initial cost in the installation of single three-phase transformers, but the individual units have certain advantages, as the breakdown of one of these is not likely to affect the others.

Referring directly to a plant in which the writer is interested, all furnaces are closed delta connected, the line voltage being equal to the individual secondary transformer voltages. In the event of the breakdown of one of these transformers, it is possible to run on an open delta. The damaged phase should be short-circuited before such operation. The cut-out of one transformer in this way reduces the current applicable to melting, to approximately 58 percent of the total normal amount. If the single case three-phase transformers are of the shell type, such operation may also be possible in the event of damage to one phase, but the likelihood of the other phases being left undamaged is comparatively small.

One of the main points of importance, as this also affects the power factor, is the directness with which the secondary power can be led from the transformers to the melting hearth of the furnace. The installation of transformers at a height above the floor level and directly behind the furnace, enables a very direct connection to be made and seems to be most advantageous.

Control of power input in Heroult furnaces is obtained by means of contact regulators operating through direct current motors, which raise or lower electrodes by means of a direct driven winch mechanism. Provision is made for a faster raising

than lowering rate, by the insertion of permanent spool-wound resistance in series with the armatures, the down contact side being provided with a greater resistance than the up or raising side. To prevent trouble through the simultaneous closing of the up and down contactors, these are mechanically interlocked with a dynamic contactor in series with the resistance, which prevents over-travel of the electrode by dynamic braking of the armature.

The contact regulators (contact making ammeters) consist of a group of three-current coils connected to low-tension slip-on type current transformers. In one of our installations these are the cotton-wound type, with permanent and variable resistance in parallel and with a capacity of three amperes, which makes the control very sensitive to current fluctuation in the furnace. It is remarkable to note the smoothness of operation obtained. Regulators of the Thury type, I believe, are very reliable, and it is claimed that they permit faster melting, but my own experience has been with the contact type exclusively, and to date we have no fault to find with these.

Briefly, then, it would seem that the electric furnace for steel making has come to stay, and it will become more and more necessary for the central station to figure upon the characteristics of operation peculiar to this type of furnace, and decide as to the desirability of the load. As improvements in a new process and its related equipment are naturally to be expected, these furnaces will undoubtedly show economies not thought possible today. The enormous strides made by the open hearth furnace bear testimony to such trend.

At the present time the electric furnace finds its principal use in the production of high-grade, uniform quality steels on a quantity basis, the size of the electric furnace averaging smaller than the commercial open hearth furnaces. Several plants have, however, adopted units as large as 35 tons, for the refining of hot metal. It is an open question whether the central station will find itself called upon to supply power for many furnaces of small size, say, 1,500 KV.A., or a lesser number of larger units.

I have only touched on electric steel furnaces for steel making. Great possibilities have been opened up, and are being constantly developed in the production of alloys, of non-ferrous metals and

a combination of ferrous metals with other alloys, as well as in the direct reduction of ores. Europe has seen more development work in this latter phase of the industry than the United States, but it may be expected that as improvements are developed and become a commercial possibility, the power requirements will be still more important.

DISCUSSION.

G. M. BERRY[1]: In connection with one part of the paper which Mr. Hess read, namely, the statement on page 422, in the third paragraph, it says that steel melted directly from a cold charge is better than that made with hot liquid metal as a charge. I would like to ask if that is based on actual observations. The concern with which I am connected has furnaces operating both with cold metal and with liquid metal as a charge, and our experience is hardly in accord with that statement. We have made a good many thousands of tons in the old original Heroult furnace, the first one operated on this continent commercially. We have had very good success with it. I really would like to get a personal opinion from somebody who is partial to the cold melt; our experience hardly coincides with the statement of Mr. Hess.

FRANK HODSON[2] (*Communicated*): Mr. Hess very rightly attaches importance to giving the central station a well-balanced load. The furnace user would find he would get much better satisfaction from the station if he always tried to keep the load well balanced; considering the increasing calls upon the central station, it is a point that the furnace user should watch very carefully. Mr. Hess put forward an excellent suggestion that graphic meters indicating power-factor should be installed on all furnace switchboards. Most of the furnace makers are now including this as part of the standard equipment, but many of the old furnaces have no power-factor meters.

I understood the paper to state that the intense temperature of the electric arc may burn the steel. If that happens it is entirely

[1] Chief Chem., Halcomb Steel Co., Syracuse, N. Y.
[2] President, Electric Furnace Construction Co., Philadelphia, Pa.

the fault of the furnace operator in not having proper slags. It is a well-known fact that steel can be heated in a vacuum or neutral atmosphere to temperatures far above ordinary commercial practice without the slightest sign of burning. It is almost impossible to burn steel except when oxidizing conditions are present. This is probably the explanation why steel can be melted under an intense arc heat without being burned. If the atmosphere is not oxidizing, steel will not burn.

Mr. Hess suggested using colored lights to warn furnace operators when they were getting sustained peaks; alarm bells have also been used, with marked success.

Personally I think more satisfaction can be obtained by designing and using furnaces that do not give these sustained peaks. Furnace users are apt to take it for granted that the melting-down period of the furnace must have sustained peaks. Our experience proves that a properly designed furnace does not give such peaks and they can be almost eliminated, even during the melting-down period.

Mr. Hess drew attention to the fact that it was not desirable to overload the furnace or try only for output. There is a very strong tendency at the present time to sacrifice quality to quantity. Probably a good deal of the rejected steel he mentioned in his paper is due to that fact. As one of the poor misguided people who have the misfortune to build electric furnaces, I am very pleased, indeed, to see the results of the Hess Company's experiments in a large furnace installation. I see from his paper that they are very well satisfied with the high quality of steel produced.

HENRY HESS[3]: One of the first points that was raised was the relative advantage, if it were an advantage, of using cold charges as against hot steel charges, charged into the electric furnace. There are several phases to that. In the first place, we must deal with human frailty and the human tendency to turn out as much stuff as you can sell, provided you can sell all that you can turn out. Now you can undoubtedly turn out more so-called electric steel when you charge into the electric furnace pre-melted steel. That pre-melted steel requires refining in the electric furnace. You may give it enough time to refine it, or you may not.

[3] President, Hess Steel Corporation, Baltimore, Md. (Father of Mr. Henry L. Hess, and responding for him.).

In other cases you may call it electric steel and merely wash it through a furnace, in which case you have electric steel, but not electric steel quality. If you put a cold charge in, you must leave it in the furnace long enough to melt it down, so whether the steel melter is conscientious or not, when he is only able to turn out cold-melted steel, he is not able to give you hot-melted washed steel. If you will use the necessary refining current, you can get good steel from even a Bessemer charge, but the certainties are that the amount of expense you are putting into current, lining loss, etc., when you are getting an equally good product, is no less when you start with Bessemer steel hot-melted than it is when you start with reasonably good scrap cold-melted. That is one reason that has governed my plant in saying that we will not put in an open-hearth furnace. We could greatly increase our capacity thus, but there is a commercial advantage is not being told "Well, this time it was not an accident, but you put one over on us, you sold us some of your open-hearth stuff for electric steel." It is well known that in Illinois they do produce electric alloy steel, and it is also equally well known that they have never yet been able, notwithstanding they put an immense expense on it, to produce a really thoroughly high-grade electric alloy steel that will compare with the high-grade crucible steels, for instance. That may be due to two factors, one is the first factor I mentioned; or it may be due to another factor, that they use 20-ton furnaces. The electric steel people generally have come to the conclusion that it is impossible to turn out a uniformly good steel from a 20-ton unit; in other words, the unit is too large; somewhere around about 8 to 10 tons is the maximum size unit that is found practicable when they want to turn out really high-grade electric steel. Now, just which of those two factors may be the cause, I cannot definitely say; I think, really, it is due to the size of the unit.

Regarding the desirability of off-peak loads, the central station man undoubtedly likes to have loads for his off-peak periods. That, however, does not seem to be really so large as it would appear. I am not basing this on my own knowledge, but I am basing it on the information I have derived from our current-furnishing concern, the Baltimore Consolidated Gas and Electric Company, which has one of the largest installations in the country.

We do receive on two furnaces—they are only 7-ton furnaces—permission to operate them on off-peak loads, which run, I think, from 10 in the evening to about 6 in the morning, and they never took a demand load on that off-peak time that we are working; in other words, no matter how much demand we are making, we do not establish a new demand. The usual thing is that if we establish a new demand during hours of operation, that operates for five years against us, the duration of the contract. That is also one of the frequent sources of friction and difference between the user and the seller of current. There seems to be a little better understanding, commercial understanding, I put it, on the part of the power companies. I have recently been able to secure a month to month demand arrangement with our supplier that they will not increase our demand for over the five years for the operation of four furnaces until some time in the late fall. Now we hope, when that time comes around, that they will continue it for another half year or so.

I am very much pleased to say that I have a point on Dr. Hering; it is not often you can get one on him, but I anticipated his use of a furnace that operates largely by the blowing of its fuse. We did that in Bridgeton; we operated a small Helberger furnace and put in a fuse that frequently blew, it blew all too frequently, but it did blow. The trouble was not that we were not using current when it was blowing, but also that we were not producing steel when it was blowing. The same thing held on our Stassano furnace. For reasons that the electrical engineers present can tell better than I can, the blowing of a fuse is attended with the rush of current, and when our fuses blew we heard from the power station promptly—it was a rather small one, and we heard from them very energetically, in fact so often that our operators simply blocked the fuses so that they could not blow. One of the gentlemen mentioned as a highly desirable thing the accomplishing of the operating of a series of furnaces on a schedule. I would like to say that if he will come down to Baltimore and show us how to do that, we will call him blessed, every last one of us. We have so far been unable to do that. We know that we can operate them on a schedule, but not economically; some steels take more refining, for one reason or another, possibly carelessness,

possibly something unavoidable, but it is there nevertheless. There would be a very distinct advantage, that has not been mentioned, if we could operate one set of furnaces as acid, with an acid lining, and then take that steel and put it into other furnaces with a basic lining for its final refining. That would be a highly desirable thing, but unfortunately we cannot operate the furnaces so that one will be ready just when the other is finished; we will always have to hold one or the other a more or less time with a consequent loss.

I think that Mr. Acheson Smith is developing a type of instrument that will make it possible to know when we are running close to the danger point of too high-peak operation, and therefore enable us to cut down a little and thus not get the high peak and thus not establish, which is the most important thing, the high demand which will then operate for five years. We would like to do that. Our central station people say that they also would like to have an instrument like that, but they absolutely insist on it that no such instrument is in existence, nor do they believe that any such instrument has ever been devised. Mr. Smith says he has one; in fact, I am commissioned here to try and get in touch with Mr. Smith, if he is present, to see how he has got along with it.

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POWER DEVELOPMENTS IN SCANDINAVIA.[1]

By J. W. Beckman.[2]

ABSTRACT.

A resumè of the development of water powers for various purposes in Norway and Sweden, showing the chronological rise of this development, and its cost, and the cost of power in those countries. A particular comparison is made between the amount of development per thousand inhabitants in Norway and Sweden and in the United States. Data for Sweden since 1913, however, are incomplete. The study is made with the object of showing how active has been the development with the Scandinavian countries, fostered by wiser legislation on the subject than in the United States. [J. W. R.]

Due to various circumstances, such as wise or unwise legislation, and due to the mental lethargy of the American people, encouraged to a great extent by the availability of cheap sources of energy other than water power, hydro-electric developments have been, to a great extent, overlooked and neglected in this country, compared with similar power sources in other parts of the world, in countries often less favorably situated as to coal supplies but perhaps more fortunate in regard to the selection of their legislating representatives.

It is often stimulating to see what other people have done along a special line and it is just as often encouraging to see how seemingly insurmountable troubles have been overcome when there was an intelligent public behind an undertaking. The two Scandinavian countries, Sweden and Norway, have been pioneers along hydro-electric developments, and it would seem of interest to get an insight into developments there.

[1] Manuscript received March 15, 1920.

[2] Metallurgical Engineer, San Francisco, Cal.

It has become a habit with us in the United States to look to Sweden and Norway, and especially to the latter, as countries favored by a kind Providence as to water power available for development and it has also become a maxim to consider that power in Norway can be obtained at fabulously low figures due to the extremely cheap cost of installation. Recent information published in a Norwegian technical journal, compiled by Mr. T. Christensen, indicates a decided discrepancy in our assumptions.

We, in the United States, compared with Norway, are very backward in the development of our hydro-electric possibilities. In our country we have unutilized possibilities which are surrounded by opportunities for the utilization of the power such as Norway never has had, and knowing the topography of that country, it is doubtful if they will ever have opportunities as we have them here today. There is no reason to deny the fact that Norway has had some extremely cheap power installations, but in many cases, and perhaps in all of them, the consumers that wanted the cheap power had to move into a desolate wilderness or to an isolated point on the coast line and there install the power-consuming industry.

It might be considered that the power could be transmitted from the generating station to a suitable point for consumption, but in many cases the formation of the country prohibits such transmission lines. Snow-capped mountains, glaciers and climatic conditions form barriers which often eliminate the possibility of long-distance transmission. These are some of the factors which determine the building of hydro-electric plants for industrial purposes, and without knowing all the details connected with the Norwegian developments it is impossible to fully comprehend their locations. It can be said, with a reasonable amount of correctness, that the larger, readily available, cheap power developments have all been taken up and are being utilized for industrial purposes, electrochemical, electro-metallurgical, as well as in the manufacture of wood products.

The estimated average cost to install hydro-electric power in Norway today is 700 Norwegian crowns, or in dollars with normal exchange, when $1.00 equals 3.75 crowns, this would make the cost of installation $194 per installed kilowatt. The investing public of Norway seems to be satisfied with a lower rate of return

than that of the United States, since this power is obtainable at the bus-bars at $19.41 per kilowatt year, and this price supposedly covers all costs such as depreciation and amortization of the plant, as well as operating expenses. The transmission cost is apparently large, since the average price of power at the end of a transmission line is $29.33 per kilowatt year, while the charge of power to the small consumer through a distributing system is $53.33 per kilowatt year. Even these figures are low compared with prices charged under similar conditions in the United States. None of the transmission lines in Norway are of any unusual length.

The water-power developments in Norway show a most interesting history and indicate what a financially poor country with a small population can do if it is fully brought to realize the advantages Nature has placed in its grasp. Here it is worth mentioning that the industrial developments of all kinds in the Scandinavian countries are due, to a great extent, to the foresight and vision of the daily papers, which are keen and eager to give to their readers authentic articles on technical and scientific matters—the only way by which a true public interest can be created for the intelligent industrial development of the country.

The first use of Norwegian water power was for the purpose of operating grist mills, flour mills and saw mills. The annual development of water power for such purposes has gone slowly forward at the rate of about 1,500 H. P. per anuum.

In the seventies, about fifty years ago, the mechanical paper mills were started and later the chemical paper mills were introduced, and this gave a fresh impetus to water power developments. During the twenty years elapsing between 1895 and 1915 the average annual water development due to the paper industry amounted to 15,500 H. P.

In 1895 only 700 to 800 H. P. electric energy was generated by water; this was the birth of hydro-electric developments.

During the following five years the total increase of water power developed for the production of electric energy amounted to 15,000 H. P., or an average increase of 3,000 H. P. per year. During the following five-year period 40,000 H. P. of water-generated electric energy was installed, and there was an average annual increase of 8,000 H. P. 160,000 H. P. additional electric

energy was placed in operation during the five-year period from 1905 to 1910, averaging an annual increase of over 30,000 H. P.

It is of especial interest that simultaneously with the increased demand for water power for the purpose of generating electric energy, the water had also been utilized in ever-increasing amounts in the paper industry and in 1910 the two interests, the electrical industry and the paper industry, were consuming about the same amounts: 214,000 H. P. by the paper industry, and 213,000 H. P. for the generation of electric energy.

At that time, one-third of the electrical energy generated was used for domestic purposes and two-thirds was absorbed by industrial demands.

During the following eight years Norway made enormous strides in the electrochemical industries, and, consequently the growth of the power-generating industries has been stupendous. In 1910, 15,000 H. P. was consumed in electrochemical industries; in 1918, 770,000 H. P. The domestic demand for power has not grown at all in proportion with that of the industries, and is today represented by a very small percentage of the total.

Sweden is a strip of land approximately the same size as the Pacific Coast States of the United States, dotted all through its length with various industries which have developed their own source of power as one of the inherent parts of their industrial activity, considering the power from the same viewpoint which prompts the development and operation of their own sources of iron ore and charcoal for the iron industries. The power is as much a raw material as any of the other components which make the industry possible, and the cheapest source for power is therefore sought and put into use.

In many parts of the United States an industrial development suffers because enormous power corporations dominate the electric field with a network of transmission lines, covering the country. These corporations, with their generating facilities, are enormous assets to the country as a whole, but, due to many circumstances, they are forced to charge exorbitant prices, exorbitant when considering the power as a raw material essential to an industry.

It is, of course, to the power corporations' interest to see as few of the small power opportunities developed as possible, and

today, owing to the activities of these corporations, a new industry contemplating starting operation asks first this question, in this connection: "Where is the nearest power line"? while in Sweden and Norway under the same conditions the question is, "Where is the nearest source of power that can be developed?"

The result of this attitude in Sweden is indicated by the following official table of 1913,* showing use or developments and number of developments in Sweden, and in a marked way shows the position of the small developments. These statistics are undoubtedly much improved since that time, both as to small and large developments. Some very large installations made by the government have since been placed in operation, and these, together with small ones, have increased the total water power developments in Sweden, since 1913, over 30 percent.

Size of Equipment in Turbine H. P.	Number of Plants	Total Number of Turbine H. P.
50,000 or more	1	80,000
25,000 – 50,000	2	68,000
10,000 – 25,000	6	109,000
5,000 – 10,000	18	116,000
1,000 – 5,000	126	245,000
200 – 1,000	296	132,000
		750,000

The following table indicates the uses the power was put to in 1913:

Utilization of the Water Powers for Different Purposes.

	Number of Turbine H. P.	Percentage
Iron industry	215,000	29
Paper and pulp industries	240,000	32
Textile industry	40,000	5
Electrochemical industry	90,000	12
Power distribution and miscellaneous	165,000	22

Very radical changes have taken place since then in the Swedish iron industry as well as in the electrochemical field. Electric pig

* On promising this paper, later detailed data were expected from Sweden, but unfortunately had not arrived when the paper had to be ready for the press.

iron manufacture has grown rapidly, and 70,000 H. P. is used in these furnaces alone, while in 1913 there were only a comparatively few thousand horsepower used in this industry. The consumption of electric energy for electrochemical manufacture in Sweden in 1917 was 126,000 H. P., and it has grown considerably since then.

It may be interesting to compare the water power reserves of the Scandinavian countries—the two European countries that are most richly endowed—with those of the United States of America. Norway has an estimated potential water power of 7.5 million horsepower, or 3,020 horsepower per 1,000 inhabitants. Sweden has an estimated potential water power of 6.2 million horsepower, or 1,050 horsepower per 1,000 inhabitants. The United States has, according to the latest estimates, a maximum of 67 million horsepower and a minimum of 37 million horsepower, or roughly, 540 and 290 horsepower respectively per 1,000 inhabitants.

As to developed water power, comparative figures are still more interesting. Norway has a population of 2.5 million people and the total developed power for all purposes is 1.25 million horsepower, or 0.5 horsepower developed for each inhabitant. In Sweden there is a population of about 5.5 million people with the total developed power of 1.1 million horsepower or 0.2 horsepower developed for each inhabitant.

In the Pacific Coast States, Washington, Oregon and California, there are 941,000 horsepower developed for all purposes, and in these States there is a population of approximately 5 million people, or 0.188 horsepower developed for each inhabitant. If hydro-electric power were developed at the same rate on the Pacific Coast as in Norway, 2.5 million horsepower would be developed, which would mean that close to one quarter of all available power was at work. Similar figures for the United States as a whole are of no real interest, since topographic conditions in the countries are so completely different.

Comparisons may be odious but they may also be of a stimulating nature. These comparisons indicate how power developments have been pushed in the Scandinavian countries, showing how the power before being developed might have been considered a luxury, and, on being developed, became a national necessity and a national asset of the highest value.

The Scandinavian countries suffer in a marked degree from shortage of fuels. Wood is practically the only native source of fuel, and as an energy source it is practically prohibited. On this account, water power developments are there of primary importance, more so than in a country where there are abundant available sources of suitable fuels for the generation of energy, as in the United States of America where coal and oil have been plentiful. But, in America, as in all other parts of the world, the true conservation is that which is applied in the Scandinavian countries, making the "White Coal" work, by the fullest development of all water power sources both large and small. Each one has its own field, and each development is as legitimate and essential as the other.

San Francisco, California.

DISCUSSION.

C. TOWNLEY[1]: Many of you know that one of the principal reasons for the slowness in developing water power in this country has been a defect in our federal laws. A very large percentage of our undeveloped power is in the West, where the federal government is a large owner of the land, and under our present law no government official has authority to grant a permit to use that land for the development of power except one that is revocable at will by the Secretary of the Interior. Some years ago a large number of permits were revoked by the then Secretary of the Interior, thus showing investors that it is not safe to put money into water power enterprises under existing laws. For the last ten years or so efforts have been made to have the defects in these laws remedied, and at the present time a bill has been passed by the House of Representatives in Washington, and the same bill, in a little different shape, has also been passed by the Senate. It is now in conference in a committee of the two Houses, which is endeavoring to reach an agreement, and if this bill should become a law, water power may be developed throughout this country with no governmental handicap.

[1] President, Am. Inst. of Electrical Engineers.

J. W. BECKMAN (*Communicated*): Since the presentation of my paper on "Power Developments in Scandinavia," I have received from Sweden later official data showing the water power developments there up to the end of 1917, and the following table indicates that development:

Size of Equipment in Turbine H. P.	Number of Plants	Total Number of Turbine H. P.
0 199	311	36,686
200 499	200	61,049
500 999	107	73,768
1,000 4,999	134	285,508
5,000 9,999	19	125,065
10,000 19,999	6	76,710
20,000 49,999	7	184,910
50,000	3	261,400
	787	1,105,096

The most interesting feature of the condition in Sweden is that of this total, 514,030 H. P. were developed by the industry itself consuming the power. In other words, half of the power generated in Sweden is generated as a part of an industry, just the same as a mine or any other source of raw material is acquired and developed for an industry. Of these 514,030 H. P., 303,711 H. P. was converted into electric power, while the remainder, 210,319 H. P., were used as mechanical power.

I think that the future hydro-electric developments of the United States have three courses to follow:

1. The development shall be done by power corporations, as is done to such a great extent now, who will sell the power to the consumers.

2. The power shall be developed by the federal government, the State or the municipalities, and with our dread of government ownership it is doubtful that this possibility will even be considered for a very long time.

3. The industries shall develop their own power sources. To me this is the only logical and economical way for the greater part of our future hydro-electric developments to follow. The power corporations cannot sell the power to the large consumer at as low a rate as at which the consumer, in most cases, can develop and produce his own power. Figures from Sweden bear

this out very startlingly. The cost of power supplied by a power corporation in Sweden is close to two and one-half times as large as what power costs industries that have developed their own power.

A judicious development of water powers by the industries themselves would assist to some extent, to distribute industries all through the country in more advantageous surroundings than they are operated under now. The big cities cannot but affect adversely the workers both physically and mentally, while small, well planned industrial cities close to the water power source cannot but have an excellent mental, moral and physical effect upon the workers as well as their families, and become economic and political assets of great value to the nation.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, C. Townley in the Chair.

LOCATION FOR A NEW ENGLAND ELECTROCHEMICAL PLANT.[1]

By C. T. MAYNARD.[2]

ABSTRACT.

A description of the cascades of the Androscoggin at Rumford Falls, Maine, with an analysis of the drainage area, impounded water in reservoirs, and uniformity of flow. Comparisons of minimum and maximum flow are made with other large water powers, showing Rumford Falls to have a relatively much larger minimum flow, with less seasonal variations. The advantages of the location as to accessibility, comfort of living, and cheapness of power are emphasized. [J. W. R.]

It is generally understood that an electrochemical industry requires 24-hour, low-priced power in large quantity and a location comparatively near the large industrial centers of the country. The great industrial activity of the United States lies principally in a zone between the cities of Boston, Albany, Buffalo, Cleveland, Detroit, Chicago, Pittsburgh, Philadelphia and New York and where in that area is there cheap hydro-electric power already developed and yet unused?

Niagara, of course, offers tremendous additional power possibilities but apparently the joint governments will not permit much more of this power to be developed for some years to come. Only recently a large steam plant had to be erected in the Buffalo district to meet the existing industrial demands, and recently on the Canadian side the Hydro-electric Commission has been facing a serious power shortage. As far as most of the other hydro-electric plants in or near this zone are concerned, even with their

[1] Manuscript received March 8, 1920.

[2] Engineer, Rumford Falls Power Co., Rumford, Maine.

efficient operation brought about by interconnection with one another they find it necessary to supplement their generating capacity during low-water periods with large steam auxiliaries in order to meet their primary power demands.

There is, however, one striking exception to the above condition and that is within 200 miles of Boston and 425 miles from New York by railroad. The writer refers to the hydro-electric plant of the Rumford Falls Power Company of Rumford, Maine. The town of Rumford, having a population of about 10,000, is situated 80 miles north of Portland on the Androscoggin River. At this point the river drops 180 feet in a series of falls extending over a distance of about one mile.

Previous to 1892 little or no use was made of this power, situated as it was in a wilderness 20 miles from the nearest railroad connection, but at that time, through the far-sightedness of the late Hugh J. Chisholm, who saw the possibilities at Rumford Falls, developments were started along the wooded banks, and today there exists a thriving community, centering largely in the paper industry, consuming 32,000 twenty-four hour horse-power from the falls.

The water power at Rumford is developed in three stages. The lowest fall of 30 feet is used, up to 85 percent of the low-water flow by six turbines of the Oxford Paper Company. The middle fall of 50 feet is used, up to 100 percent of the low-water flow, by thirteen turbines of the International Paper Co. At these two developments the Power Company leases the water to the paper companies and the latter use it principally in direct drive for beaters, grinders and paper machines, although some of this energy is converted into electric power for mill uses.

The upper or 100 foot fall is developed by a modern hydro-electric plant with a present maximum generating capacity of 24,000 kw. which can be very easily and quickly increased to 31,500 kw. by the addition of another 7500 kw. unit, space having been reserved for this additional unit, and the tunnel, from the gate house to the turbine location in the station, already completed. The hydro-electric development, as a whole, is recent in design and construction, having been completed only within the past few months. A detailed description of the plant will not be given here, as that has been done in two recent issues of the technical

press. Sufficient to say that it is as near correct installation as the best engineering and unstinted money could make it.

The present week-day load on the Rumford Falls Power Station averages about 9600 kw. for the twenty-four hours, with a maximum demand rarely exceeding 10,500 kw., giving a load factor of about 92 percent. The load is divided approximately as follows: 7000 kw. to the paper industry, 2200 kw. to a ferro-silicon plant, and the remainder to the Rumford Falls Light & Water Company, a public utility supplying electric service for 2500 light and small power users.

Of course, it is obvious that no hydro-electric station, however well designed, can produce reliable, continuous power unless the water is always available to drive the water turbines, and this brings us to a discussion of the existing hydraulic conditions. Back of the Rumford Falls Power Station the Androscoggin drains a territory of 2090 square miles (5435 sq. km.), and back at the headwaters there is a comprehensive chain of lakes, including the Rangeley system, and reservoirs with an area of 125 square miles (325 sq. km.) impounding between 29 and 30 billion cubic feet (800,000,000 cub. m.) of water. This storage, combined with hundreds of square miles of wooded lands, provides Rumford Falls as well as the several other powers on the Androscoggin with a stream-flow regulation probably unequaled by any other river of like size. Nor is this all, for if future plans are carried out and increased power demands it, there will be constructed additional water storage with a capacity of 7½ billion cubic feet (200,000,000 cub. m.) giving an ultimate storage of 37 billion cubic feet (1,100,000,000 cub. m.).

The splendid regulation of the Androscoggin at Rumford since the construction of the storage may be better understood when it is noted that the minimum daily flow in the year is consistently 2000 second-feet (57 cub. m.-sec.), although it has on rare occasions dropped as low as 1500 second-feet (43 cub. m.-sec.), and the usual maximum flow about 15,000 second-feet (426 cub. m.-sec.). Yet on June 18, 1917, following an unprecedented rainfall of 8¾ inches in 12 days, the flow reached only 30,000 second-feet (854 cub. m.-sec.), billions of cubic feet being caught and held in storage.

Even more impressive in showing the regularity of the flow of the Androscoggin, as compared with the flow of some of the other noted power rivers in New York State and New England are the following figures based on extreme minimum and maximum flow records:

River	Location	Square Miles Drained	Minimum Flow in Sec. Ft. per Sq. Mile Drained	Maximum Flow in Sec. Ft. per Sq. Mile Drained
Genessee	Rochester	2,360	0.05	19.0
Mohawk	Cohoes	3,400	0.13	21.0
Hudson	Spier Falls	2,800	0.24	30.0
Connecticut	Brattleboro, Vt.	6,300	0.24	24.0
Androscoggin	Rumford	2,090	0.72	14.0

Above Rumford Falls comparatively still water sets back for several miles, and as a result troubles due to anchor ice are reduced to a minimum and below the hydro-electric plant the middle falls carries the water rapidly away, giving a tail-water elevation varying through the year not over 4½ feet (1.35 m.). The head-water elevation at the plant has an extreme variation of only about 4 feet (1.2 m.), rising and falling with the tail-water, thus maintaining a very uniform effective head. Even during the unusual flood period of June, 1917, the head-water rose only about 7 feet (2.1 m.) and the tail-water about 9 feet (2.7 m.).

Unlike most large American hydro-electric developments, the Rumford Falls system has no high-tension lines reaching out for hundreds of miles and subjecting the station apparatus to the possible dangers of damage due to "shorts," grounds, high-frequency surges and lightning disturbances incidental to long distance transmission; it has only 5 miles (8 km.) of well-protected 11,000 volt line. Consequently load disturbances due to these hazards are not much in evidence.

Perhaps you may ask, "Why is not this unused, developed power transmitted to the markets that are nearer the coast and which could absorb it all?" The answer is this: the power is already available in a thriving town, not too far away from the great markets and adaptable to further growth. Freight facilities are good, the town is healthfully and beautifully located, with excel-

lent schools, good trading facilities and all those things that combine to make a place desirable for men to build their homes. In Rumford there are available excellent industrial sites at very reasonable rates.

The Power Company believes that, if possible, the power should be used locally, rather than transmitted to the distant markets, for the reason that growth at Rumford would be stimulated, more reliable power can be delivered, as the hazards of transmission would not be encountered, and cheaper power could be furnished, as the overhead and maintenance expenses of a large transmission system would be eliminated. Just now the Rumford Falls Power Company has developed and ready for immediate use approximately 35,000,000 kw. hours per year of continuous primary power and 40,000,000 kw. hours per year more of secondary power and, furthermore, this power can be purchased at a rate believed to be lower than can be offered anywhere else in or near the great industrial centers of this country.

Summing up, the writer asks where is there today a more attractive location for an electrochemical industry, demanding five to seven thousand kilowatts of low-priced reliable power, than in Rumford, Maine?

Rumford, Maine,
March 4, 1920.

DISCUSSION.

O. G. THURBER (*Communicated*)[1]: We are working more or less in the dark where the value of intermittent run of river power to the electrochemical industry is concerned. In planning the development of our southern rivers, which have a very variable flow, the engineer must decide on the size of his ultimate development, and this naturally depends upon the value of the intermittent power to prospective users. After having paid for the dam, water rights, flooded lands and many other charges which are included in the cost of the hydroelectric development, the cost of providing for an additional turbine is of no great consequence. The cost

[1] Chief Engineer, Alabama Power Co., Birmingham, Ala.

of the total installation of this additional turbine might not amount to over say $25 or $30 per killowatt. Power from it might be available for an average of, say, 100 days per year, or say 2,000 hours per year. What the hydroelectric engineer would like to know is whether or not the electrochemical engineer can pay him a sufficient amount to justify his expending the money required for this additional installation.

It appears to me that it is a question of cost of storing raw materials and the handling of labor so that the electrochemical engineer who has a process which requires raw materials of low cost, very little labor and very little plant cost, can make use of power which the hydroelectric engineer must otherwise run to waste.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, C. Townley in the Chair.

WATERPOWERS OF THE PACIFIC COAST.[1]

By F. H. Fowler.[2]

That our fuel supplies are by no means as inexhaustible as they have been popularly regarded, and that in the not far distant future we shall have to depend upon our streams for much of the power needed in our industries, appears at last to have dawned on the American public. Rising prices and the difficulties of maintaining an adequate fuel reserve have done more in three short years to bring about this awakening than was accomplished by the warnings of experts in the preceding decade. The utilization of our waterpowers has become one of the most pressing questions of the hour.

The estimate of the potential waterpowers of the United States prepared by the Geological Survey for the National Conservation Commission in 1908, published by the Commissioner of Corporations in his report on "Water Power Developed in the United States, 1912," and later revised and republished in Senate Document 316, 64th Congress, 1st Session, is still our most authoritative estimate of potential power for the entire country. Funds should have been provided long since for a detailed study covering the whole United States, in the manner that is now proposed for the North Atlantic States.

The following condensed tabulation from Senate Document 316, compiled on a basis of 70 percent efficiency, will bring to mind the regional distribution of our potential waterpower resources.

[1] Manuscript received April 10, 1920.

[2] U. S. Forest Service, San Francisco, Calif.

TABLE I

Potential Waterpower of the United States

District	Minimum		Maximum	
	Horsepower	Percent	Horsepower	Percent
New England	868,000	3.11	1,605,000	2.98
Middle Atlantic	1,357,000	4.86	2,488,000	4.62
East North-Central	832,000	2.98	1,604,000	2.98
West North-Central	902,000	3.23	1,956,000	3.63
South Atlantic	2,346,000	8.39	4,257,000	7.90
East South-Central	1,087,000	3.89	1,964,000	3.64
West South-Central	353,000	1.26	822,000	1.52
Mountain	8,694,000	31.11	16,131,000	29.92
Pacific	11,504,000	41.17	23,078,000	42.81
United States	27,943,000	100.00	53,905,000	100.00
Distribution of Potential Power in Pacific States				
Washington	4,932,000	17.65	8,647,000	16.04
Oregon	3,148,000	11.27	6,613,000	12.27
California	3,424,000	12.25	7,818,000	14.50
	11,504,000	41.17	23,078,000	42.81

The tabulation shows that nearly 43 percent of the maximum potential waterpower in the United States is concentrated in the three Pacific states, Washington, Oregon and California; and it is to a very general statement of conditions within these three states that the writer proposes to confine this paper.

GENERAL CONDITIONS

In no section of the United States does topography so greatly influence not only climate and power resources, but also the distribution of population and industries, as in Washington, Oregon and California. The great Cordilleran mountain system extending along the west coast of both Americas, and locally known as Sierra Nevada mountains in California and Cascade Range in Oregon and Washington, not only protects the western coastal strip in these states from the more rigorous climate of the interior, but also presents a barrier against which drift the storms and moisture-laden winds of the Pacific.

The same forces of nature that folded the earth's surface into the main ridge have thrown up minor folds to the westward,

resulting in a parallel but much lower range closer to the coast. The trough between the two ranges may be traced in a general way from the Gulf of California northwestward through all three states and across the Canadian boundary. It contains the great central valley of California, the Willamette valley in Oregon, and Puget Sound on the northwest coast of Washington.

More or less local geological upheavals have broken the continuity of this great fold in the Sierra Madre and Tehachapi Ranges south of the Great Valley of California and in the Siskiyou and neighboring ranges between the head of the Sacramento River and the headwaters of the Willamette; elsewhere it is practically continuous. In the great valleys within this trough and smaller valleys lying in minor folds, parallel in general to it, are found the most extensive areas of productive land and a large part of the population.

In California the distance from the ocean to the main crest of the Sierras is about 175 miles (300 km.); in Oregon the average distance from the ocean to the crest of the Cascades is about 120 miles (200 km.), while in Washington the distance from the ocean proper to the crest of the main ridges is about the same, but the distance from the eastern shore of Puget Sound to the crest is not more than 50 to 60 miles (100 km.).

The storms drifting from the ocean landward are deflected upward and cooled, first by the Coast Range, which robs them of a portion of their moisture, and then by the main Cordillera, on the slopes of which they drop most of their watery load. Records show a more or less uniform increase of precipitation with elevation on the western slopes of the Sierras up to a certain elevation, which in California appears to be about 7,000 feet (2,100 m.), east of which there is a gradual decrease in mean annual precipitation to the crest of the ridge, and then a very rapid decrease.

The relative temperatures of the atmosphere over land and sea differ not only with the season, but with latitude. The land is, in general, cooler than the sea in winter, and warmer in summer. Since the prevailing atmospheric drift is eastward at all seasons, there is, due to the above conditions, a marked seasonal variation in rainfall, or a "wet season" and "dry season" each year—little rain falling from May to November. This variation is far more marked in the south than in the north.

Mean annual precipitation at different points in the Pacific states varies between the widest limits found in the country. At certain points on the coast of Washington and Oregon the mean annual rainfall runs as high as 133 inches (338 cm.); but as we proceed southward along the coast there is a continuous decrease, until in the vicinity of San Diego the mean annual rainfall is but 9.56 inches (24 cm.).

The lowest mean seasonal precipitation in the region is found in the desert country of southeastern California, where at times no rain has fallen for several years in succession. The mean recorded at one of the stations in this area is but 2.34 inches (6 cm.), as compared to 133 inches (338 cm.) on the northwest coast, and a maximum of 150 inches (381 cm.) in the neighboring mountains.

From the Canadian boundary southward through the Cascade Range to the Lassen Peak region in California the mountain structure is chiefly volcanic, consisting of lavas, basalts and extensive areas of ash and pumice. In the Feather River basin, south of Lassen Peak, geologic conditions change, and from that point southward there are but limited areas of distinctly volcanic origin, and the main ridge of the Sierras consists almost entirely of granites, with lower slopes of andesites, shales and serpentine.

Extreme variation in the amount and seasonal distribution of rainfall, as well as wide differences in geology and topography, result in wide differences in stream flow. From Feather River northward there is in general an increasing tendency toward uniformity in river discharge, while from that point southward the character of the streams becomes increasingly torrential or "flashy." In northern Washington, perpetual snows and extensive glaciers in the upper mountains, as well as the volcanic structure of the country, tend to maintain a high rate of discharge during the dryer seasons of the year, and also to mitigate the severity of floods. Farther south the perpetual snow fields and glaciers decrease in size, and therefore contribute a far smaller amount to the low-flow of the streams, finally disappearing entirely. Storage, therefore, becomes increasingly important from north to south, the amount of storage necessary in comparison with the utilized stream flow also increases, and, lakes being less numerous than in the north, the unit cost of storage is generally higher.

The foregoing remarks refer entirely to streams originating chiefly or entirely within the three coast states. There are, however, two extremely large interior streams which find their outlet to the Pacific Ocean—first, the Columbia, draining much of our northwest, breaking through the mountains to the westward and forming the boundary between the states of Washington and Oregon; and, second, the Colorado, draining the heart of the west and southwest, taking its course southward into the Gulf of California, and forming, in its lower course, the boundary between southeastern California and Arizona. The general conditions within their basins are too varied to be treated in this paper. There is far more power in the Columbia basin than in any other drainage in the country. It is estimated that more than two and a quarter million horsepower are available at major sites in the Colorado basin.

OPERATING AND MARKET CONDITIONS

California hydroelectric systems are now operating waterpower plants with a combined capacity of about 543,000 K.V.A., and steam auxiliaries with an additional capacity of 285,000 K.V.A., a grant total of 828,000 K.V.A., or 1,110,000 horsepower. The combined installation in hydro plants of Washington and Oregon is about two-thirds that in California.

Throughout the coast there is a power shortage, due to low water and to the rate of installation not having kept pace with the growth of load. This shortage will be most acute this year in California, which is practically 200,000 K.V.A. behind in hydroelectric installation. Plants under construction aggregate about 165,000 K.V.A., but will not be in operation until the last months of 1920 or the beginning of 1921. In the low-water season of the coming fall, every available steam-standby will be in operation, plants which have been on the junk list will be resuscitated, and the consumption of fuel oil, which in 1919 reached 4,895,000 barrels (500,000 metric tons), will be greatly augmented. In June and July, 1919, the months of maximum demand that year, the total load on the California hydroelectric systems averaged 419,000 K.V.A., of which 116,000, or 27.7 percent, was carried by steam auxiliaries. The mean load on the California systems has increased very steadily at the rate of about 35,000 K.V.A. per year.

The average load carried by most of the hydro plants is under 60 percent of their rated capacity, and an annual increase of 35,000 K.V.A. in mean load would therefore necessitate an annual installation of at least 60,000 K.V.A. in hydroelectric generating machinery, after the present deficiencies are made up. In short, California should have a total installed hydro capacity of 800,000 K.V.A. by 1921, and an annual increase of 60,000 K.V.A. each year thereafter, to adequately handle the normal increase in load.

If large electrochemical, electrometallurgical or railway loads are developed, the rate of increase will be proportionally greater.

Detailed figures for the growth of load in Washington and Oregon are not now available, but are being collected by the National Electric Light Association. Unless new power uses are developed within the two states, the growth in load will hardly be as rapid proportionally as in California.

FEASIBLE SITES AND PROSPECTIVE DEVELOPMENTS

The estimates given in Table I serve merely as a basis for regional comparisons of potential power. Far more detailed studies have been completed on certain drainages by the Federal and State Governments, municipalities, and engineering and public utility companies. Most of the Puget Sound streams and those in southern Washington have been studied in detail by the United States Geological Survey in co-operation with the state of Washington. Results already published show a total of 232,000 horsepower without storage and 391,000 with storage for the Cowlitz, Nisqually, Puyallup, White, Green and Cedar Rivers, draining the territory between Portland and Seattle, north of the Columbia and east of Puget Sound. Similar studies show an average minimum of 389,500 (since found to be somewhat high) horsepower for the Klickitat, White Salmon, Little White Salmon, Lewis and Toutle Rivers, draining into the Columbia from the north, between the mouth of the Cowlitz and The Dalles. The Yakima, which drains the basin east of the Columbia, will produce only 12,000 horsepower continuously, but 105,000 horsepower may be developed during the irrigation season. Natches River, principal tributary of the Yakima, will yield 57,530 horsepower continuously without storage, and 97,950 horsepower with storage, while its mean for the irrigation season, with storage, is 160,500 horse-

power. Clealum River, another tributary of the Yakima, will yield 4,770 horsepower without and 21,560 horsepower with storage.

Some of the sites included in these estimates are already in process of utilization, and more complete studies are being made of others. It will, of course, be many years before the streams will be fully developed on the plans outlined.

Among the most important power developments is the proposed municipal system of the City of Seattle on the Skagit River, in the extreme northern Puget Sound drainage. Carried to completion, this system will comprise 200,000 or more horsepower.

Developments located at Priest, Kettle, and Rock Island Rapids and The Dalles on the main Columbia have been proposed from time to time, but investigations of power possibilities at The Dalles appear to have been carried farther than for the other sites.

A detailed report of power available at The Dalles was prepared by co-operation between the State and Federal Governments, in 1913.[3] The project contemplated the development of power at Five Mile Rapids, near The Dalles, 90 miles (144 km.) east of Portland and 187 miles (300 km.) above the mouth of the river. The minimum recorded flow at this point was 41,900 cubic feet (1,186 cubic meters) per second, and the maximum 1,170,000 cubic feet (33,000 cu. m./second). At an average low water discharge of 50,000 second-feet (1,415 cu. m./second) the estimated net head was 105 feet (31 m.); and at a high water discharge of 800,000 second-feet (22,640 cu. m./second), 45 feet (13.5 m.). It was estimated that 480,000 horsepower could be developed practically continuously, and that there would be 120,000 more available for eleven months, an additional 100,000 for ten months, and still 100,000 more for eight months, giving a total development of 800,000 horsepower that might be considered economically justifiable by stream flow conditions. It was estimated that the cost would be $104 per horsepower for a development of 480,000 horsepower, $62.50 per horsepower for 800,000 horsepower, or $46.30 per horsepower on the basis of the total rated capacity of generators (1,080,000 horsepower) that would have to be installed in order to secure the continuous output of 800,000. The plant

[3] "The Columbia Power Project," Bulletin No. 3, accompanying Fourth Biennial Report, State Engineer John H. Lewis, Jan. 11, 1913, by L. F. Harza, Project Engineer.

would operate at its full capacity during only four months of the average year.

By way of comparison, only 150,000 horsepower is installed at the great Keokuk plant, and 498,000 in all plants on both sides of the river at Niagara Falls.

It was estimated that with only 480,000 horsepower marketed at The Dalles, and the plant financed by sale of 6 percent securities at a 10 percent discount, cost of power would be $15.13 per horsepower year, allowing for a proper depreciation and maintenance fund, but no profits to the company making the development. This price was also based on the assumption of an immediate market for all power. Further estimates show that "if, however, the surplus power of 320,000 horsepower could be sold at rates equivalent to 80 percent of the price of the continuous primary power for eleven months' service, 60 percent for ten months' service and 30 percent for eight months' service, then the selling price of primary power under conditions as above would be reduced to * * * $11.02 for 6 percent securities sold at 10 percent discount." The report on the project covered in detail the various possible outlets that could be found for the great amount of energy available, and the result showed that neither existing nor prospective industries would justify construction of the great plant. The most logical power market for a development of this size would be as a supply for a large electrometallurgical or electrochemical industry, and the study disclosed that the site was so handicapped by remoteness from sources of raw material and from market that it would not prove under present conditions a commercial success. The only possible justification for this development from an electrochemical standpoint was found to be for the manufacture of ammonium nitrate.

The state engineer of Oregon has made tentative studies of other large projects on the Columbia, Snake, Deschutes, Rogue and Klamath, capable of continuous output of 2,401,000 electric horsepower.

A tabulation of proposed developments in California prepared by the writer in October, 1919, showed a combined proposed installation of 2,100,000 K.V.A. Many well-known possibilities were not included. It appears, therefore, that the state's potential supply is ample for years to come.

THE ELECTROCHEMICAL OUTLOOK

That the very large waterpowers of the Pacific coast will eventually be utilized as a source of energy for electrochemical and electrometallurgical industries none can doubt, but the date of their utilization is highly uncertain. Were unit cost of construction the only possible deterrent, many large developments would be under way today. Availability of raw materials and the market for the finished products are the most serious handicaps. The results of investigations carried out in connection with the Columbia River project are, unfortunately, general in their application. In connection with that project, industry after industry was investigated as a possible outlet for large blocks of power, and abandoned as probably unprofitable under prospective market conditions. That the site is one of the most wonderful in the country cannot be denied, but its development is for the future, and not the present.

The earliest development of extensive electrochemical and electrometallurgical industries on the Pacific coast will probably be on Puget Sound, where there is ample waterpower susceptible of development at relatively low unit cost, in moderate-sized units, and in such close proximity to tide water as to minimize transmission costs and losses. The Columbia River and lower Willamette near Portland, offering similar advantages but to a less conspicuous degree, may be expected to follow in turn. The writer does not anticipate that California will ever compete with her northern neighbors on a large scale in electrochemical manufacturing for export (especially in those branches of the industry where power cost is a large percentage of the total cost). Its manufacturing for the local market will probably far exceed that in the other two states. Natural conditions in California lead to high unit costs in hydroelectric installations, especially where long trunk transmission lines are included. In order to get the most favorable power rate, it would therefore be necessary to establish the electrochemical industry near the generating station, which may be from 90 to 175 miles (144 to 281 km.) from tide water, with consequent higher freight charges and shipping difficulties. If, on the other hand, these transportation difficulties are avoided by establishing the industry on tidewater, the cost of

power will be considerably greater. Market alone will determine whether a given industry can flourish despite these conditions.

Probably the lowest power rate yet quoted in California is $2.50 per kilowatt per month for 24-hour power, based on the maximum average demand for a 15-minute period. This rate was established for the encouragement of electrochemical and electrometallurgical industries other than re-melting. It is granted at the option of the power company or upon order of the California Railroad Commission. The base rate is subject to an additional charge of 6 cents per kilowatt maximum demand for each 1 percent that the average power factor falls below 90 percent. A general surcharge since allowed by the Railroad Commission to take care of increase in all generating costs, permits an additional charge of 0.2 cent per kilowatt hour. The net cost per horsepower year therefore ranges from $35.45 for 90+ percent power factor and 100 percent load factor, down to $32.84 with 90+ percent power factor but only 80 percent load factor.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

THE ELECTRICAL PRODUCTION OF ALLOYS.*

By RALPH M. MAJOR.[1]

ABSTRACT.

Account of producing alloys in two Heroult furnaces having different electrode regulating equipment, and their effects on the working of the furnaces. Also a discussion of the general advantages of electric melting as compared with any other furnace. Detailed description of the manufacture and properties of nickel-chromium-iron (Nichrome) alloy, nickel-chromium (Kromore) alloy, nickel-manganese (Mangaloy) alloy, nickel-chromium-steel alloy, nickel-steel (Climax) alloy, and nickel-steel (Invar) alloy.

[J. W. R.]

This paper will describe the alloys produced electrically at the plant of the Driver-Harris Company, Harrison, New Jersey. An interesting fact about the alloys is that they are not only produced electrically but that their chief uses are found in electrical appliances, so that they may be described as "Alloys Produced Electrically for Electrical Uses."

The electrical equipment for melting these alloys consists of two Heroult furnaces, each having a capacity of two tons. One of these furnaces has been in operation for two years, while the other has just recently been installed. The only difference between these is that the older furnace is equipped with Westinghouse standard equipment[2] while the newer furnace is equipped with General Electric standard equipment.

The difference in these standard equipments is mainly in the transformers and in the automatic electrode regulators. The

* Manuscript received March 14, 1920.

[1] Metallurgist in charge of Research Laboratories, Driver-Harris Co., Harrison, N. J.

[2] A full description of this equipment was published in "Electrical World," August 17, 1918.

Westinghouse equipment has a transformer bank of 800 k. v. a., in two units, while the General Electric has one unit. The Westinghouse automatic regulator is the Thury and the General Electric is the Seed.

The fundamental difference between these regulators is the manner in which the contact is made with the motor that moves the electrode. In the General Electric regulator, contact is made direct by means of a floating lever of a contact-making ammeter. This contact is made with a high-speed motor and the electrode takes its new position in one quick movement. The Thury regulator makes the contact with the motor by means of a mechanical device, electrically controlled. This consists of a floating lever arm carrying knife edges, which engaging with dogs controls an arm that engages or disengages in slots in a rocker arm through which motion is transmitted to the contactors for the motor that moves the electrode to its new position. These contacts are only momentary and are really impulses to the motor. The change in position of the electrode is therefore very slight for each contact. The electrode takes its new position, therefore, in a series of short movements. The rocker arm is operated by an independent motor and these mechanical parts are moving continuously. This results in considerable wear of parts, therefore requiring many replacements. The hand control of the Thury regulator is by means of drum controllers, while the General Electric has the push button control.

The furnaces are the 3-electrode 3-phase type. The current is supplied by the Public Service Company, as 2-phase, 2200 volts, and is changed to 3-phase, 110 volts by our transformers.

At the start of a melting operation the voltage is kept up to 100-105 volts, but after the charge is in a molten condition, the voltage may be lowered to 50 volts, thus giving a shorter arc with less heat radiation from the arc. This results in a saving of the refractories.

The electrodes used are 12-inch (30 cm.) carbons in five foot (1.5 m.) lengths. The ends are bored and tapped and are united by means of studs, as in Fig. 1. This arrangement results in less breakage than where electrodes are made in male and female parts as in Fig. 2. The electrode consumption including breakage is fourteen pounds per ton of alloy produced.

The kilowatt hours per ton of alloy produced is 700 to 750. This seems high when compared to what is considered good practice in melting steel, but it must be remembered that our melting units are comparatively small when compared to steel units and our furnaces are not run continuously, so that we have heats on cold bottoms every day instead of only once each week; in addition to this, the refining of our alloys requires a higher temperature than for steel.

The melting time required for the first heat from a furnace is four and one-half to five hours, while the second heat on a hot bottom can be finished in three and one-half to four hours.

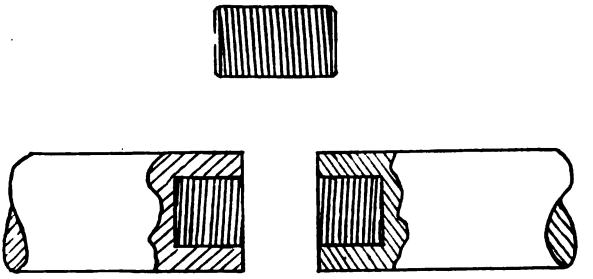

FIG. 1.

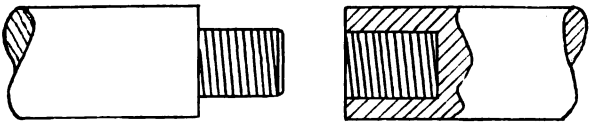

FIG. 2.

The furnaces are basic lined. One reason for this is that the furnaces are not run continuously and when this is the case a basic lining is the only one practical.

The furnace temperature at the end of run will be from 3200 to 3300° F. (about 1800° C.) at tapping time. The pouring temperature is about 2900° F. (1600° C.). The life of linings and roofs is very short. When we get twenty-five heats to a roof, we are well satisfied.

The molten alloys are tapped from the furnace into a bottom-pour ladle and teemed into cast-steel split molds, having a clay hot-top. These molds are split across the corners, so that if any

fin adheres it will be on the corner of ingot and not across the surface. The ingots are 4 x 5 inches (10 x 12.5 cm.), tapered, and weigh about 150 lb. (68 k.).

Some of the advantages of melting these alloys in an electric furnace are as follows:

1. A higher temperature is produced than can be obtained in any other kind of a furnace, and this temperature can more easily be controlled. This high temperature results in:

(*a*) A more rapid melting of the charge.

(*b*) The ability to tap the superheated metal into a bottom-pour ladle and allow it time to remain so that the deoxidizers added to the metal as it streams into the ladle are given a chance to get in their work and the impurities given a chance to rise into the slag, while the metal chills only enough to come down to the proper pouring temperature.

(*c*) Extremely hard requirements on the refractories. This can be helped a great deal by proper regulation of the size of the arc near tapping time, and also by the condition of the slag. A very thin slag that presents a mirror surface and reflects most of the heat to the roof, will do much damage.

2. The atmosphere in which the melting takes place is more nearly non-oxidizing, and therefore a greater saving of valuable additions, such as manganese, is possible.

3. A more perfect quality and a more nearly perfect homogeneity of product is possible in melting with an electric furnace than in any other way.

It has been stated that with the use of an electric furnace, perfect quality and absolute homogeneity of product are assured. I wish to say here that an electric furnace alone is not the panacea for all melting ills. It is true that a melter who understands his business can make a better product in an electric furnace than in any other furnace; but it is also true that I have seen just as poor a quality of steel poured from an electric furnace as was ever tapped from an open hearth.

The ingots, after stripping, are sent to the chipping room where all surface defects are eliminated and then hammered to a two-inch square billet. These billets are then hot rolled to ¼-inch (0.63 cm.) rods from which they are cold drawn to the finished

sizes of wire. The Driver-Harris Company has not reached the point of using electric annealing furnaces, but it is hoped that before long the annealing process can be included in a description of the electrically produced alloys herein described.

The alloys to be described are as follows: 1. Nichrome, 2. Nichrome II, 3. Kromore, 4. Mangaloy, 5. No. 193 Alloy, 6. Climax, 7. Invar.

1. The alloy *Nichrome* is a 60 percent nickel, 12 percent chromium alloy containing about 25 percent of iron. This alloy is cold-drawn to any size wire or cold-rolled to ribbon form. In these forms it is much used in electrical heating appliances in which the heating elements are run at a maximum temperature of 1800° F. (982° C.). The physical properties of this alloy are as follows:

Specific gravity 8.15; Weight per cubic inch 0.29 lb.

Ultimate tensile strength 100,000 lb. per sq. in. (70 kg./sq. mm.)

Specific heat 0.111 over the range 0 to 100° C.

Co-efficient of linear expansion 0.0000116 per degree C. over the range 0° to 100° C.

Thermal conductivity 0.0326 cal. per cm., per sq. cm. per 1° C. per second, made with ¼-in. (0.63 cm.) diameter section. This value is one-fifth that of soft iron.

Electrical resistivity 660 ohms per circular mil-foot at 23° C. (110 micro-ohms per cm. cube).

Temperature coefficient of electrical resistivity: 0.000026 percent per degree C., or 0.000014 percent per degree F. (These values were made over a range of 20° to 50° C.).

This alloy *Nichrome* is also produced electrically for the purpose of pouring castings. The value of these castings is in their property of resisting heat. They do not scale at high temperatures, do not corrode, and are highly resistant to the action of ordinary acids and alkalis. A very large tonnage of this material is used in carburizing boxes, lead pots, cyanide pots, and various kinds of retorts. It was this material *Nichrome* cast into large tubes 15 in. (38 cm.) inside diameter, and 13 ft. 6 in. (400 cm.) long that made it possible to produce the excellent grade of charcoal that made the gas masks of our soldier boys so superior to the other masks used at the end of the late war.

This same alloy *Nichrome* is now produced in still another form. It is known as forged *Nichrome*. Some of this is rolled into sheet or forged into conveyor-chain links operating at high temperatures. Many of the large gas and oil-engine builders are now using this material for engine valves.

The various uses of *Nichrome* are covered by a number of patents issued and pending.

2. *Nichrome II* is a nickel-chromium alloy having a higher chromium content and a smaller iron content than *Nichrome;* the iron being only about 12 percent, or half that in *Nichrome*. This material will stand a slightly higher working temperature than *Nichrome* giving very satisfactory results in heating elements operating at 2000° F. (1093° C.). The electrical resistance and temperature coefficient of this material are practically the same as that of *Nichrome*.

3. *Kromore* is a nickel-chromium alloy entirely free from iron. It is practically an 85-15 mixture. It is furnished in the form of wire and ribbon, and is recommended for use at extreme temperatures and for open-type heating units.

The electrical resistivity is 580 ohms per circular mil-foot at 24° C. (96 micro-ohms per cm. cube). The temperature coefficient of electrical resistivity is 0.000050 percent per degree C., or 0.000028 percent per degree F.

4. *Mangaloy* is a high-nickel manganese alloy containing about 40 percent iron. This alloy drawn to wire has a high electrical resistivity but does not withstand oxidation as well as the nickel-chromium alloys. The electrical properties of *Mangaloy* are as follows: Specific electrical resistance at 20° C. is 644 ohms per circular mil-foot (107 micro-ohms per cm. cube). Its temperature coefficient of electrical resistivity is 0.000073 percent per degree C., or 0.000041 percent per degree F.

The above named alloy is patented.

5. *No. 193 Alloy* is a 30 percent nickel steel, having a small content of chromium, about 1.5 percent. This alloy gives very satisfactory results at an operating temperature up to 1000° F. (537° C.) and is an ideal cheap material for use in open room heaters operating at black heat. It has a specific electrical resistance at 24° C. of 525 ohms per circular mil-foot (87 micro-ohms

per cm. cube). Its temperature coefficient of electrical resistivity is 0.000014 percent per degree C., or 0.000008 per degree F. It has a coefficient of linear expansion of 0.0000171 per degree C.

6. *Climax* is also a nickel steel. It, however, contains only 25 percent nickel and no chromium. It, therefore, does not resist oxidation as well as No. 193 alloy and corrodes slightly; but it is used satisfactorily when cheap material is needed and resistance is the only consideration. The specific electrical resistance at 20° C. is 500 ohms per circular mil-foot (83 micro-ohms per cm. cube). The temperature coefficient of electrical resistivity is 0.000186 percent per degree C., or 0.000103 per degree F. The coefficient of linear expansion is 0.0000171 per degree C.

7. *Invar* is an alloy steel containing about 36 percent nickel. This material is rolled into strip and is valuable because of its extremely low coefficient of linear expansion being only 0.000000295 per degree C.

CONCLUSIONS.

In conclusion it might be said that probably a greater variety of electrically produced alloys for electrical purposes is made in the electric furnaces of the company with which I am connected than in the furnaces of any other alloy manufacturer. All furnace heats are made under careful chemical and metallurgical supervision. Chemical analyses and micro-photographs are made of each heat, and the materials are closely followed through all annealing and drawing processes. Finally, every coil or spool of wire or ribbon that is shipped must pass rigid inspection for gage, conductivity, resistivity and freedom from all surface defects.

Bloomfield, N. J.
March 12, 1920.

DISCUSSION.

S. A. TUCKER[1]: About what is the temperature at which nichrome is forged?

R. M. MAJOR: The temperature is rather high for forged nichrome. Nichrome is now being used in the manufacture of auto-

[1] Chemical Foundation, Inc., New York City.

mobile and marine hydro-engine valves, forging it around the temperature of high-speed steel.

F. S. WEISER[2]: I would like to ask Mr. Major for a little information in regard to the physical properties of nichrome. I have been informed that its ultimate tensile strength is about 48,000 pounds per square inch, and that if heated to a temperature of 800° C. it still retains an ultimate tensile strength of about 24,500 pounds. It is an important metal in some metallurgical operations. I would like to know how it would behave at a temperature of about 650° C. and whether nichrome sliding on nichrome at 650° C. would abrade very rapidly. Is there any such information available? Also, what would be a safe stress to put upon nichrome at a temperature of about 800°C., or in other words, what is the yield point?

R. M. MAJOR: There has not been any very accurate test made yet on nichrome; do you speak now of castings?

F. S. WEISER: Yes, I am speaking of castings.

R. M. MAJOR: Work on castings at increased temperatures will be done very shortly. There have been several attempts at it, but nothing has been done in an accurate manner yet. Speaking of the wear, nichrome is not unusually hard and will not stand much wear. The ordinary forged nichrome has a Brinnell test of about 170 as it comes from the hot rolls; it can be hardened to about 255 by cold working; it cannot be hardened by any heat treatment.

Tensile tests on nichrome castings recently made show the following results:

Cold—50,000 lb. per sq. in.	35 kg. per sq. mm.
800°C—23,000 to 25,000 lb. per. sq. in.	16-20 kg. per sq. mm.
1000°C—17,000 lb. per sq. in.	12 kg. per sq. mm.

[2] Asst. to Supt., Elec. Trans. Dept., Scovill Mfg. Co., Waterbury, Conn.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

THE ELECTROLYTIC PRODUCTION OF CALCIUM.*

By P. H. Brace.†

Abstract.

This paper is a record of some of the results of an experimental investigation of the electrolytic process for the production of calcium. The work was done at the Research Laboratory of the Westinghouse Electric and Manufacturing Company.

Of the various types of cells experimented with, three proved of particular interest. Of these, two were patterned after those described by other writers and the third and most successful cell was a modification developed in the course of this investigation.

The operation of these cells is described and their inherent disadvantages pointed out.

The characteristics of several electrolytes are discussed, and a means of preparing a satisfactory electrolyte is described. The results of this work indicate that pure calcium chloride, properly treated, is the best electrolyte.

Introductory.

The review of the literature indicated that there were two general types of cell which showed the most promise, and that they could be developed so as to provide a simple and easily manipulated means of preparing moderate quantities of metallic calcium of a good degree of purity. The first cell constructed followed in a general way the idea of Goodwin.[1] This type of cell will be referred to as the submerged-cathode type. The second cell was of the type described in the later writings of Goodwin,[2]

* Manuscript received January 17, 1920.

† Research Chemist, Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.

[1] See references at end of paper.

and by Johnson,[4] Frary, Bicknell and Tronson,[5] and others. This cell will be designated as the moving-cathode type. The third and most successful cell was a modified form of the moving-cathode type in which most of the disadvantages of the others have been eliminated.

Submerged Cathode Cell.

Figure 1, drawn to scale, represents the cell first experimented with. The theory of its operation is that the calcium will be deposited on the tip of the submerged, water cooled, cathode in

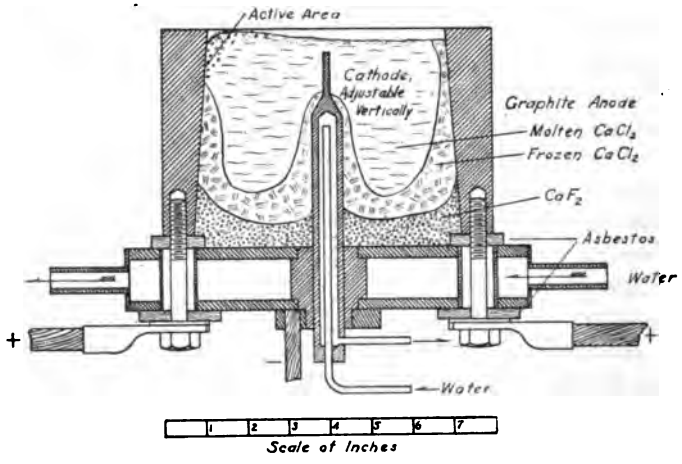

FIG. 1. Submerged Cathode Cell.

a molten condition, and form globules which will rise to the surface of the bath by reason of their relatively low specific gravity. These molten globules may then be ladled out and cooled in oil according to Goodwin's procedure, or they may be impounded within a water-cooled ring at the surface of the electrolyte, coalescing to form larger masses. Several runs were made with this cell, using various currents between 75 and 150 amperes, and some metal was recovered by Goodwin's method. No success attended the attempts which were next made to secure larger aggregations of metal by collecting the molten drops within a water-cooled copper ring just in contact with the surface of the molten electrolyte. Were the apparatus to be constructed on a

sufficiently large scale this might prove a practicable method. Under our conditions the temperature of the electrolyte had to be so high in order to prevent the cooled ring from freezing the whole surface of the bath that any calcium formed was quickly dissipated by reaction with the bath and the atmosphere. The largest pieces of calcium secured from this cell were roughly spherical in shape, and approximately two centimeters (0.8 in.) in diameter. All were more or less porous and cracked badly when attempts were made to work them into wire or sheet. The principal reason for the poor quality of the yield was that the molten calcium was not in equilibrium with the bath of molten electrolyte in which it floated. If a globule were allowed to remain in the cell for a few minutes it would be almost completely dispersed by the reaction that went on. This effect may have been due to chlorine entrained in the electrolyte, to the formation of the sub-chloride whose existence is asserted by Wohler and Rodewald,[2] or to the dispersion of the metal into the electrolyte in a colloidal or semi-colloidal condition. In this last case the metal would be rather quickly converted back to normal chloride by the chlorine evolved at the anode. The author's opinion is that a colloidal suspension of calcium in the electrolyte was formed. This view is supported by the observation that when globules of calcium were allowed to remain in the electrolyte while it solidified, and subsequently broken out, the portions of the electrolyte nearest the globules were of a violet color and gave off gas, presumably hydrogen, when dissolved in water. The remainder of the electrolyte had a grayish cast and dissolved in water with no evolution of gas. Apparently calcium diffuses away from the globules in contact with the bath and is soon oxidized or converted to chloride. The above considerations indicate the desirability of keeping the area of contact of the calcium and electrolyte as small as possible. The disadvantages of the type of cell described above are apparently inherent, and grow out of the fact that the conditions of deposition and collection are such as to keep the metal-electrolyte contact area large.

Moving-Cathode Cell.

It was concluded that the moving-cathode type of cell, which will now be described, was more susceptible of improvement.

The cell which was constructed was of the type described by Goodwin,[3] and later in more or less modified forms by other writers, including Johnson,[4] and Frary, Bicknell, and Tronson.[5]

In this type of apparatus a graphite cup functions as a container for the electrolyte and as anode. The calcium is deposited in the form of a roughly cylindrical stick upon a water-cooled cathode which is gradually moved vertically upward as the accumulation of metal increases. The cathode current density is so regulated that the surface of the calcium in contact with the bath is kept molten. The surface tension of the liquid metal prevents the formation of nodules or spongy deposits, and very little electrolyte is entrained. The outstanding difficulty is the variability of the temperature of the electrolyte resulting from uncontrollable changes at the anode.

As a rule only a portion of the circumference of the anode was active. Changes in the position and extent of this active area went on constantly, and in a very erratic manner, causing the temperature of the electrolyte to fluctuate for two reasons; first that the direction of the convection currents produced in the bath by the evolution of chlorine were changed, causing the molten electrolyte to sweep over fresh, cooler surfaces, and second because the changes in anode current density which resulted changed the voltage drop across the cell, and consequently the rate of heat liberation in it. The cathode current density required to keep the lower end of the deposit of calcium molten is a function of the temperature of the electrolyte, and it may be controlled by variations in the current, the rate of advance of the cathode, or both. In general it was controlled by the second method because it was found that constant current operation was the most satisfactory. When the temperature of the electrolyte was low a relatively high cathode current density was required. This was secured by increasing the rate of advance of the cathode, thus decreasing the area of contact between the deposit of calcium and the electrolyte, and also the diameter of the deposit of calcium. Conversely, a high temperature of the electrolyte necessitated a slower rate of cathode advance and resulted in the formation of a deposit of greater diameter. Thus the uncontrollable changes

at the anode caused great variations in the diameter of the sticks of calcium which were produced, and made the operation of the cell rather difficult.

Several runs were made with a cell of this type in which a water-cooled graphite container like that shown in Fig. 2 was used, and the product secured was much more satisfactory than that obtained from the submerged-cathode cell. It was successfully rolled into rod and small sheets. The uniformity of the product both as to size and quality left much to be desired however, the sticks varying greatly in section and purity.

Considerable practice was necessary before one could produce calcium with a reasonable expenditure of time, energy, and materials, and this was the principal reason for discarding this cell as unsatisfactory.

Modified Cell.

With these facts in mind, the modified form of cell, represented by Fig. 2, was developed in an attempt to overcome the difficulties. A considerable degree of success has attended these efforts.

In the figure the essential parts of the cell proper are drawn to scale, and the electrical connections shown diagrammatically. Referring to the lettering on the figure, A was an Acheson graphite pot containing the electrolyte, B, B'. The pot was not in electrical connection with any of the other parts of the cell. It was screwed into a water-cooled cast iron block, C, and surrounded by thermal insulation, D, consisting of lamp-black rammed between it and a sheet iron casing, E. Thus the principal cooling effect was from below, and the tendency for thick, troublesome crusts to grow out over the surface of the electrolyte from the sides of the container was greatly reduced. The approximate contour of the portion of the cell contents which was solid during operation is indicated by B' on the figure. The deposit of calcium, Q, was started on a round-ended iron nut, F, screwed to a copper block, G, which was supplied with cooling water through concentric tubes, as indicated. Electrical connections were made at the upper end of this cathode structure. Movement of the cathode was produced by means of a small shunt-wound, direct-current motor, not shown, geared to a nut, not shown, whose rotation raised or lowered the screw H. Speed regulation was secured by varying the resistance in series with the field of the motor. The anodes, I, I', were of Acheson

graphite, and were bolted to water-cooled brass blocks, J, J', to which electrical connections were made. They were independently adjustable, both vertically and horizontally, in a vertical plane.

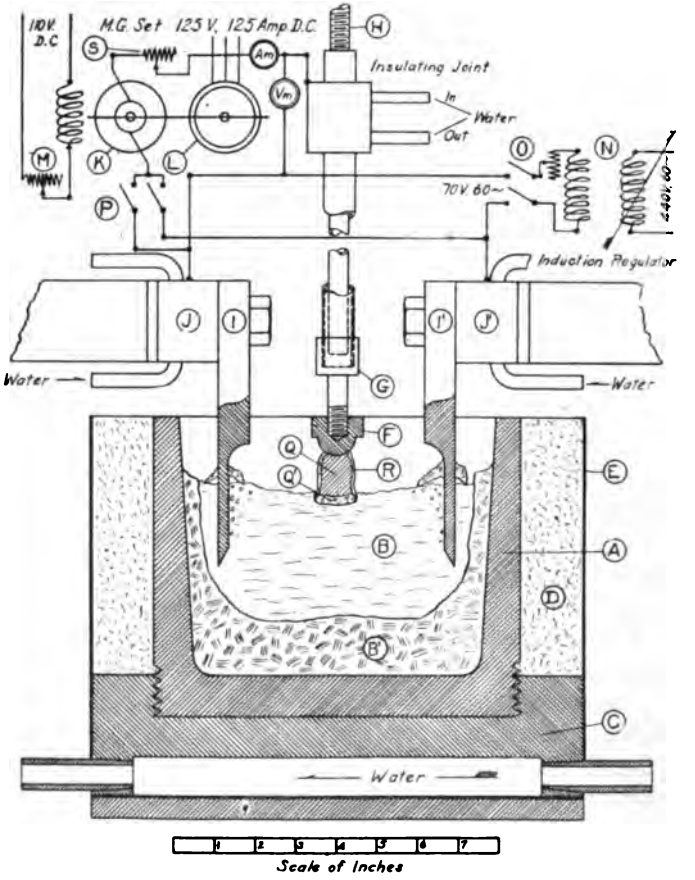

FIG. 2. Modified Moving Cathode Cell.

The current for electrolysis was furnished by a 250 volt, 117 ampere, Type SK Westinghouse direct-current generator, K, direct connected to a 440 volt, 60 cycle, 25 horsepower Westinghouse synchronous motor, L. The excitation, and consequently the output of the generator was controlled by a rheostat, M, in series with a 110 volt, constant potential supply. A ballast resist-

ance, S, of 0.1 ohm was placed in series with the cell. The generator was called upon to deliver as high as 200 amperes for periods of several hours duration, and while it became rather warm there was no indication that it had suffered from its 70 percent overload operation. A 60-cycle, single-phase induction regulator, N, was employed to furnish current for heating the bath and adjusting its temperature just previous to electrolysis. The voltage was stepped down from 440, and could be adjusted to any value between 24 and 90.

Operation of Cell.

Commencing with the cold, empty cell, the scheme of operation was as follows: The flow of cooling water to all water-cooled parts was first verified. The generator was placed in operation and its voltage on open circuit adjusted at approximately 75; the voltage on the secondary of the induction regulator set at approximately 80; and a small amount of electrolyte placed on the bottom of the graphite pot, A. Switch P being open, switch O was closed, making the anodes I, I', the terminals of the secondary circuit of the induction regulator, N. The anodes were brought into contact at their tips, and then slightly separated, striking an arc which soon melted a pool of electrolyte into which they were then dipped. Thereafter, the current passed through the molten salt, heating it rapidly, and quickly melting down the additional amounts which were charged. The level of the electrolyte was brought to within approximately 2.5 centimeters (1 inch) of the top of the cell. Some electrolytic action went on during this process in spite of the use of alternating current. There was a small evolution of gas at the electrodes, and more or less black scum, which was apparently finely divided graphite, appeared on the surface of the electrolyte. This scum was cleared off before commencing electrolysis, as experience showed that it reacted vigorously with calcium if given opportunity.

When the bath had been brought to the proper temperature and skimmed, the tip, F, of the cathode was brought to within a fraction of a centimeter of its surface. Switch O was then opened, shutting off the heating current; switch P was closed, placing the cell in communication with the generator with the anodes in parallel with the positive pole; and contact between the cathode

tip, *F*, and the electrolyte was made and broken, establishing an arc which was allowed to burn for a few seconds before contact was again made and electrolysis commenced. The purpose of the arc was to heat the iron tip of the cathode momentarily to a temperature above the melting point of calcium, so that the metal first deposited would wet a considerable area and so insure good thermal and electrical contact.

As soon as electrolysis began the current was adjusted to the desired value, usually near 200 amperes, and the cathode motor started. Some little experimenting was required during the first few minutes in order to determine the correct cathode speed. Slight changes in conditions within the cell usually necessitated occasional small adjustments of the rate of cathode movement during the run, but runs have frequently been made without such adjustments, all changes being compensated for by the movement of the anodes. Once started, electrolysis usually continued rather uneventfully until the limit of motion of the cathode was reached. The electrolyzing current was then shut off by opening the switch, *P*, and heating current again passed by closing the switch *O*. The deposit of calcium, *Q*, was removed by unscrewing the nut, *F*, and was stored in an air-tight container. Fresh quantities of electrolyte were then charged and melted down as described above in order to make up for the losses, and after screwing a fresh cathode tip in place electrolysis could be proceeded with as before.

At the conclusion of a series of runs the electrolyte was replenished; the anodes removed from their holders while the bath was still molten, and stored in air-tight containers, and the cell covered with a closely-fitting lid. Thus protected, the outfit has lain idle for considerable periods and has been put in service again on short notice with no difficulties.

During the course of the electrolysis the attention of the operator was required to keep the electrolyzing current uniform to within one ampere, and to maintain the correct cathode conditions. The phenomena at the tip of the cathode were the chief criteria for judging the performance of the cell. The operator soon learned to interpret these appearances and to correct any undesirable tendency before the conditions in the cell had become unfavorable. When the cell was operating properly the electrolyte in the immediate neighborhood of the cathode was at a consider-

ably higher temperature than in the bath as a whole. The cathode was the center of an irregular, bright rosette formed by the currents of hot liquid moving away from it. The evolution of chlorine at the anodes caused two vigorous streams of electrolyte to flow toward the center of the cell from opposite sides. The cathode was placed where the opposing streams met and formed a comparatively quiet area. An ample supply of cool electrolyte was thus insured, and there was little tendency to wash away the liquid calcium, Q' from the end of the cathode. The thickness of this liquid layer was kept small—approximately two millimeters—and not allowed to extend more than a very short distance above the general level of the electrolyte. As the deposit was drawn from the bath, it became covered with a transparent layer of solidified electrolyte, R, which effectually protected it from the atmosphere. The silvery surface of the metal could be seen through the coating.

When the temperature of the electrolyte became too low the tip of the cathode was not maintained in the liquid state, and the calcium was deposited in the form of a voluminous sponge, whose growth, if not interrupted, would soon cause short circuiting of the cell. As soon as any tendency toward subnormal temperature was noted it was counteracted by raising the anodes slightly. This increased slightly the voltage drop across the cell, and an immediate rise in the temperature of the electrolyte followed. If for any reason a spongy deposit did start to form, the remedy was a quick elevation of the cathode through a short distance. The current density and the voltage drop at the cathode were thus greatly increased, and the local temperature rise which resulted soon melted the sponge and permitted the restoration of normal operation. The spongy deposit grew very rapidly so that prompt action was necessary, in order to prevent serious disturbance of the operation of the cell.

When the temperature of the electrolyte became too high, the boundary between the molten and solid portions of the deposit moved upward, rising above the general level of the bath. The molten metal clung to the cathode like a drop of water to the end of a rod, and was moved about by the surface agitation, and the protecting layer of chloride melted and drained away. Oxidation then took place, the heat evolved making a bad matter worse. In

extreme cases the molten calcium apparently assumed a spheroidal state with reference to the electrolyte, and the local temperature rise became very rapid. Very quick work was then required to prevent the formation of an arc which would melt off several centimeters of the deposit.

Excessively high temperatures were remedied by lowering the anodes, thus decreasing the anodic current density and the voltage drop across the cell, and producing an immediate fall in the temperature of the electrolyte. The slightly increased immersion of the cathode, resulting from the rise in the level of the electrolyte caused by the increased anode displacement, worked in the right direction. In extreme cases, such as the appearance of the spheroidal state, it was necessary to quickly lower the cathode a short distance and momentarily interrupt the electrolyzing current. This procedure usually restored normal operating conditions. Obviously the proper thing to do was to prevent the occurrence of extreme conditions requiring radical measures for their correction. A little experience taught the operator to correctly judge the tendency of the cell and to control it accordingly, and then the outfit described worked smoothly enough.

A fine spray of electrolyte was produced during the operation of the cell and was carried away by the draft used to dispose of the chlorine. This loss accounted for a considerable portion of the total consumption of electrolyte. When pure calcium chloride was used no difficulty was experienced due to the deterioration of the electrolyte with continued use. After considerable use, the cold electrolyte had a slight grayish case, owing to the presence of small amounts of finely divided graphite from the anodes. The wear of the anodes was small, and the principal part of it occurred while the alternating current was being used for melting the electrolyte.

The "anode effect" observed by other workers was never evident during normal operation. It could be produced at will by raising the anodes until the current density had exceeded a certain critical value. It appeared as a bluish glow covering the submerged portions of the anodes. The appearance of this effect, which is undoubtedly due to the formation of a nearly continuous film of gas between the anode and electrolyte, was accompanied by a sudden rise in the voltage across the cell.

The product made by the cell just described was in the form of nearly cylindrical rods, approximately 35 centimeters (14 inches) long, and 7.5 millimeters ($\frac{1}{3}$ inch) in diameter. The diameter of the deposits varied somewhat from one run to the next, but it was usually possible to keep it constant to within two millimeters during any one run.

In the description of some of the experiments on other cells it was noted that the uncontrollable changes in the anode conditions resulted in variations in the electrolyte temperature, rate of advance of the cathode, and section of the deposits. In the cell now under consideration the provision of definite, controllable anode areas has made it possible to use the previously uncontrolled anode changes to compensate for the changes produced by variables still beyond our reach. The resulting apparatus is very much easier to operate, and produces a very much more uniform product than any other cell which was investigated.

Electrolytes Used.

Various electrolytes are recommended in the literature, among which are the eutectic mixture of calcium chloride and calcium fluoride[6] (containing 16.5 percent of CaF_2) and mixtures of calcium chloride and potassium chloride[7] containing up to 25 percent of the latter. The underlying idea seems to be that an electrolyte of very low melting point is desirable. The writer's experience has indicated that the melting point of the electrolyte should not be greatly below that of the calcium, for two reasons: first, that an electrolyte of very low melting point will drain away from the hotter portions of the cathode under normal conditions and allow oxidation to take place, and second, that an electrolyte far above its melting point is very mobile, and therefore the escape of the chlorine induces such rapid circulation that proper deposition of the metal is interfered with. Both of the electrolytes noted above exhibited the defects mentioned. The operation of the cell was very difficult when they were used. The calcium fluoride-calcium chloride mixture had the additional disadvantage that the escaping chlorine made a foam on the surface of the bath which interfered greatly with the control of cathode conditions.

The writer's conclusion is that pure calcium chloride, properly dehydrated, is the most satisfactory electrolyte.

Preparation of the Electrolyte.

These investigations have indicated that proper dehydration of the calcium chloride is essential to the best performance of the cell. The first supplies of calcium chloride were from the J. T. Baker Chemical Co., and were labeled, "Calcium Chloride, C. P. Anhydrous." The behavior of the material during fusion indicated that it was far from anhydrous. Much bubbling and spitting occurred. When this material was electrolyzed, a considerable amount of gas was evolved at the cathode. This gas ignited as it escaped, and burned with little puffs of intensely yellow flame. No coherent deposits of calcium could be secured under these conditions. Fusion of the material in a gas-fired furnace in an Acheson graphite crucible previous to placing it in the cell did not help matters greatly. The molten chloride was cast into ingots in iron molds after it had been maintained well above its melting point for fifteen minutes. Considerable amounts of gas were evolved during solidification of the ingots, and many blow-holes were found along the axes of all the ingots. A strong odor of hydrochloric acid was noted.

If electrolysis of this material was continued long enough the cathodic gas evolution gradually decreased and the bath became more workable. This procedure was so clumsy and inefficient, however, that a better process of dehydration was sought for, working on the assumption that the disturbing factors were traces of water remaining in the fused material, and hydrocarbons absorbed during the treatment in the gas furnace. It was thought that these impurities might be eliminated by treating the highly heated electrolyte with metallic calcium. Experiment showed that calcium reacted with the molten chloride when they were vigorously stirred together with an iron rod at a temperature of 900° to 950° C. Small bubbles of gas were given off which burned at the surface of the melt with a yellow scintillation that recalled the yellow flames previously seen at the cathode when the material was electrolyzed. The stirring was continued until the melt had cooled to the pasty stage. Small amounts of gas were still being evolved. The chloride was then reheated to a temperature somewhat above its melting point, with further stirring, and cast into cold iron molds. It solidified with no evolution of gas, forming translucent, well crystallized ingots of

a grayish cast. No gas was given off at the cathode when these ingots were melted down in the cell and electrolyzed, and very satisfactory deposits of calcium were obtained.

Further experimentation showed that a satisfactory electrolyte could be obtained by dissolving the pure chloride in a little water; adding a few percent of ammonium chloride; boiling the solution down as far as possible and completing the dehydration in a muffle at approximately 400° C.; and previous to electrolysis treating the fused salt in the cell with a small amount of metallic calcium. This was the procedure finally adopted.

Characteristics of the Product.

When the knack of operating the cell last described had been acquired, very satisfactory deposits of calcium could be easily obtained. These were nearly circular in cross section, approximately 35 centimeters (14 inches) long, and 7.5 millimeters ($\frac{1}{3}$ inch) in diameter. It was found possible to keep their diameter constant to within two millimeters throughout a run, and some deposits showed greater uniformity of section than this.

Rod, wire, and sheet were readily produced by forging and rolling. These operations could be conducted with the material either hot or cold, though in the latter case brittleness developed when extreme reductions were attempted. A brief annealing near 350° C. removed this brittleness and permitted further reduction. Between 300° C. and 400° C. the calcium was softer than lead and extremely plastic. Under the hammer or rolls it became covered with a thin, dense coating of oxide which greatly retarded atmospheric attack.

Analysis showed a chlorine content of 1.08 percent, and very small quantities of carbon, which latter was no doubt derived from the anodes. The specific gravity of a cold-rolled rod was found to be 1.46, and the resistivity to be 6.77 microhms per centimeter cube at 22° C.

Conclusions.

(1) The results of an experimental investigation of the electrolytic production of calcium have been described. Three types of cell were experimented with: (a) The submerged cathode cell described by Goodwin: (b) The moving-cathode type described

by Goodwin and others; (c) A modified form of (b) developed in the course of this investigation. The conclusion reached is that the last mentioned cell is far easier to operate than either of the others, and that the product is much more uniform.

(2) The use of electrolytes containing salts other than calcium chloride is discussed. and the disadvantages of these mixtures are pointed out. It is concluded that pure calcium chloride makes the best electrolyte.

(3) Proper dehydration of the chloride was found to be essential to the successful production of calcium. The results of experiments with variously treated lots of chloride are presented, and the process finally adopted is described. A feature of this process is the elimination of disturbing impurities by treating the electrolyte with metallic calcium just previous to electrolysis.

Deposits of calcium nearly uniform in cross section were produced. These showed a chlorine content of 1.08 percent, a resistivity of 6.73 microhms per centimeter cube at 22° C., and a specific gravity of 1.46. The material was easily worked into various forms by the usual metal working processes.

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Research Laboratory,
Westinghouse Elec. and Mfg. Co.,
January 10, 1920.

DISCUSSION.

T. D. YENSEN[1]: I understand that calcium has been found useful in connection with telescopes, to take up moisture that condenses on the lenses due to changes in temperature.

P. H. BRACE (*Communicated*): Dr. P. T. Nutting of this laboratory has made experiments which indicate that calcium may be an effective and safe desiccating agent for use in telescope tubes.

[1] Research Laboratory, Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

ELECTROLYTIC CHROMIUM.[1]

By GEORGE J. SARGENT.[2]

ABSTRACT.

Brief allusion is made to the history of the deposition of chromium, including some unpublished work done by Skillman at Cornell University. Details are given of the electrolysis of various mixtures of chromic sulphate and chromic acid, showing that the yield of chromium from chromic acid solutions is greatly increased by the addition of chromic sulphate. Tabulated records of experiments with rotating cathodes, as compared with stationary cathodes, and investigations of the most favorable temperatures, and strengths of solution and mixtures, and current densities. Some theorizing is indulged in concerning the deposition of chromium with two different valences, 3 and 6, from chromic acid, chromic sulphate plating solutions. Very good deposits of chromium were obtained from chromic acid solutions containing small amounts of chromic sulphate. Low temperatures yielded fair ampere-hour efficiencies at comparatively low current densities. A deposit up to 1.25 centimeters thick was obtained. The chromium plating is extremely resistant to corrosion by air, moisture, and many chemicals. [J. W. R.]

Chromium may be deposited from various chromous solutions, but the use of a diaphragm is necessary and it is difficult to obtain good deposits or to keep the composition of the catholyte constant. The work of Carveth and Curry[3] indicated that the most promising solutions for the deposition of chromium were chromic acid solutions, from which fair deposits can be obtained quite easily and without a diaphragm.

[1] Manuscript received February 22, 1920.

[2] Res. Chemist, New York City.

[3] Jour. Phys. Chem. (1905), 9, 353.

HISTORICAL.

The earlier investigators of the deposition of chromium from chromic acid solutions were concerned principally in determining whether chromium could actually be deposited from chromic acid solutions. Carveth and Curry[3] cleared things up by showing that a very high current density was required to deposit chromium from chromic acid solutions and that the yields of chromium were greatly increased by the addition of small amounts of mineral acids.

Skillman, in some unpublished work done at Cornell, investigated the deposition of chromium from chromic acid solutions containing sulphuric acid. He used a platinum anode and a rotating copper cathode. The temperature of the solutions were kept at about 20° C. during electrolysis by passing cold water through a glass coil immersed in the solution. Cathode current densities in the neighborhood of 100 amperes per sq. decimeter were used. Skillman obtained his best results from a 15 percent CrO_3 solution containing 2 percent of sulphuric acid. All yields of chromium varied very considerably with electrolysis. The yields obtained at the beginning of a series of runs with a given plating solution were low and gradually increased with electrolysis until finally a maximum yield was obtained, after that the yields decreased slowly with further electrolysis.

Salzer[4] has patented a chromium plating solution containing three parts of chromic oxide to four parts of chromic acid. The plating solution may contain 5 to 25 percent of chromium. He claims to be able to obtain coherent deposits of any thickness which are harder than steel and very flexible. In a later patent[5] the activity of the plating solution is increased by adding chromic salts, as the sulphate or chloride.

EXPERIMENTAL.

The variation of the yields of chromium with electrolysis observed by Carveth and Curry and by Skillman must have been caused by a corresponding change in the composition of the plating solution. In all cases where chromium is deposited from chromic acid solutions a very considerable amount of chromic

[4] U. S. Patent 900597 (1908), Oct. 6.
[5] Ger. Patent 225769 (1909), May 13.

acid is reduced to the chromic state. Thus the electrolysis of chromic acid solutions containing free sulphuric acid, under conditions giving chromium deposits, should result in the formation of chromic sulphate until all the sulphuric acid had been neutralized. Tests showed that the addition of small amounts of chromic sulphate to C. P. chromic acid solutions increased the yield of chromium very greatly and that the yields of chromium obtained from these solutions did not increase with electrolysis. These facts show that the change in the yields of chromium with electrolysis from chromic acid solutions containing free sulphuric acid is due to the effect of the chromic sulphate formed in the plating solution.

Experiments were now begun to determine the conditions most favorable for the deposition of chromium from chromic acid chromic sulphate solutions. This proved to be anything but a simple matter as there are several factors that influence the deposition of chromium very noticeably and the influence of one factor may be greatly dependent on other factors.

Baker or Baker and Adamson's C. P. chromic acid was used in all experiments. The chromic sulphate used in nearly all the experiments was a green variety containing by analysis 27.96 percent Cr_2O_3 and 44.21 percent SO_3. This chromic sulphate dissolved very slowly in water so a standard solution was used in making the chromic acid chromic sulphate plating solutions. The amounts of chromic acid chromic sulphate in the plating solutions are calculated as $Cr_2(SO_4)_3$.

In each of the experiments given in the following four tables 100 cc. of the plating solution, in a 150 cc. beaker, was electrolyzed with a current of 2.5 amperes for approximately ten minutes. The plating solutions were cooled during the electrolysis by passing cold water through a glass coil immersed in them. The amounts of electricity passed through the solutions were measured by a copper coulometer. The cathodes were copper rods thinly chromium plated to avoid loss of copper. The anode was a sheet of platinum bent to form a hollow cylinder, in the center of which the cathode was placed.

The ampere-hour yield of chromium from salts in which it has various valences is theoretically: From chromous solutions, valence 3, 0.6458 g.; from chromic solutions, valence 6, 0.3229 g.

TABLE I.

15 Percent CrO_3 Solutions.

$Cr_2(SO_4)_3$ Added Percent	Temperature of Solution ° Centigrade	Chromium Deposited Grams	Copper Deposited Grams	Amp. Hr. Yield of Chromium Grams
0.25	9 – 9	0.0388	0.4896	0.0939
0.50	8 – 9	0.0460	0.4844	0.1126
2.00	8 – 9	0.0547	0.4877	0.1329
	20 Percent CrO_3 Solutions.			
0.00	11 – 9	0.0011	0.3945	0.0033
0.125	9 – 8	0.0327	0.4877	0.0796
0.25	10 – 9	0.0426	0.4948	0.1025
0.50	10 – 10	0.0498	0.4935	0.1196
2.00	11 – 11	0.0571	0.4967	0.1362
	25 Percent CrO_3 Solutions.			
0.25	8 – 9	0.0495	0.4873	0.1204
0.50	8 – 9	0.0539	0.4846	0.1318
2.00	11 – 8	0.0583	0.4897	0.1406
	30 Percent CrO_3 Solutions.			
0.25	8 – 9	0.0497	0.4905	0.1201
0.50	8 – 9	0.0564	0.4891	0.1367
2.00	8 – 9	0.0563	0.4918	0.1357

TABLE II.

20 Percent CrO_3 Solutions.

$Cr_2(SO_4)_3$ Added Percent	Temperature of Solution ° Centigrade	Chromium Deposited Grams	Copper Deposited Grams	Amp. Hr. Yield of Chromium Grams
0.50	8 – 8	0.0446	0.4897	0.1080
2.00	8 – 9	0.0469	0.4897	0.1136
	25 Percent CrO_3 Solutions.			
0.25	7 – 7	0.0502	0.4918	0.1206
0.50	7 – 8	0.0501	0.4918	0.1205
2.00	7 – 8	0.0393	0.4923	0.0946
	30 Percent CrO_3 Solutions.			
0.25	7 – 7	0.0358	0.4907	0.0863
0.50	7 – 8	0.0525	0.4907	0.1269
2.00	9 – 8	0.0498	0.4799	0.1230
	35 Percent CrO_3 Solutions.			
0.25	8 – 8	0.0242	0.4799	0.0598
0.50	7 – 7	0.0493	0.4876	0.1199
2.00	7 – 8	0.0484	0.4876	0.1177

TABLE III.

30 Percent CrO_3 Solutions.

$Cr_2(SO_4)_3$ Added Percent	Temperature of Solution ° Centigrade	Chromium Deposited Grams	Copper Deposited Grams	Amp. Hr. Yield of Chromium Grams
0.25	7-8	0.0255	0.4919	0.0613
0.50	7-8	0.0491	0.4919	0.1183
2.00	8-9	0.0484	0.4918	0.1166
	35 Percent CrO_3 Solutions.			
0.25	7-8	0.0255	0.4918	0.0614
0.50	6-7	0.0477	0.4833	0.1169
2.00	6-7	0.0452	0.4833	0.1109

TABLE IV.

30 Percent CrO_3 Solutions.

$CrCl_3$ Added Percent	Temperature of Solution ° Centigrade	Chromium Deposited Grams	Copper Deposited Grams	Amp. Hr. Yield of Chromium Grams
0.25	8	0.0517	0.4909	0.1248
0.50	8	0.0526	0.4815	0.1295
2.00	8	0.0452	0.4833	0.1109

Table I shows the yields of chromium obtained from solutions containing varying amounts of chromic sulphate and chromic acid when a rotating cathode was used with a cathode current density of 49 amperes per sq. decimeter. Solutions containing no added chromic sulphate gave black deposits with very low yields. The addition of even very small amounts of chromic sulphate increased the yield of chromium very greatly. For instance, the addition of only 0.125 percent of chromic sulphate increased the yield of chromium about 24 times. The yields increased with the addition of chromic sulphate up to 2 percent but the deposits obtained from solutions containing over 0.5 percent were poor. The yields of chromium also increased with the concentration of chromic acid up to 30 percent CrO_3. The best deposits were obtained from the 30 percent CrO_3 solutions with 0.25 and 0.5 percent $Cr_2(SO_4)_3$ added. These deposits were very white and quite good.

Table II shows the yields of chromium obtained with stationary

cathodes with a cathode current density of 24 amperes per sq. decimeter. The best deposits were obtained from the 35 percent CrO_3 solution with 0.25 percent $Cr_2(SO_4)_3$ added and from the 30 percent CrO_3 solutions with 0.25 and 0.5 percent $Cr_2(SO_4)_3$ added. The latter plating solution is the better solution as it gives as good deposits as the other solutions and at the same time considerably greater yields of chromium. The deposits obtained with stationary cathodes were as good, if not better, than those obtained with rotating cathodes, so the use of rotating cathodes was abandoned.

Table III shows the yields of chromium obtained with a cathode current density of 19 amperes per sq. decimeter. The yields of chromium, with one exception, were lower than corresponding yields obtained with a current density of 24 amperes per sq. decimeter. The deposits obtained also were not as good, so the effect of still lower current densities was not investigated at this time.

Table IV shows the yields of chromium obtained from 30 percent CrO_3 solutions with various amounts of chromic chloride added, with cathode current densities of 24 amperes per sq. decimeter. The effect of a given percentage of chromic chloride is somewhat different from that of the same percentage of chromic sulphate, but if the different molecular weights of the two are taken into consideration, the effect of chromic chloride is very nearly the same as that of chromic sulphate. The deposits obtained in Table IV were not as good as the deposits obtained with solutions containing chromic sulphate.

Having obtained quite good thin deposits of chromium from a 30 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution at a temperature of about 10° C. with a current density of 24 amperes per sq. decimeter, thicker deposits were attempted and difficulties immediately encountered. The chromium deposits were very hard and brittle and had a great tendency to crack. The tendency to crack was very much more apparent with thicker deposits. The material on which the chromium was plated also had a considerable influence on the cracking. Chromium plated on copper had a much less tendency to crack than when plated on chromium, but even then heavy deposits usually cracked.

In view of the fact that in general better deposits of metals are obtained from warm solutions, the deposition of chromium was

tried at higher temperatures. Qualitative experiments showed that very good deposits could be obtained at higher temperatures provided higher current densities were used. Quantitative experiments were undertaken to determine the current density necessary in order to obtain good yields of chromium.

Lead anodes were found to be superior to platinum anodes, aside from the matter of cost, in that with lead anodes the chromic acid reduced at the cathode was oxidized back to chromic acid at the anode. Thus the plating solutions could be maintained easily at a desired composition. With platinum anodes only a small amount of the chromic acid reduced at the cathode was oxidized at the cathode. On account of the very considerable effect of a slight variation of temperature on the yield of chromium, it was found necessary to control the temperature of the plating solution during electrolysis much more accurately than had been done previously.

This was done by passing water under a given head, through a heater, controlled by a constant temperature regulator, and then through a block-tin coil immersed in the plating solution. Block tin was found to be only very slightly attacked by the plating solutions and block-tin coils were much preferable to glass coils on account of their much greater heat conductivity and less fragility.

The temperature of the water flowing into the block-tin coil seldom varied more than 0.5° C. during a run and that for only a short time. The temperatures given in following experiments where ampere-hour yields have been determined were the temperatures of the water entering the block-tin coil. The actual temperature of the solutions at the cathodes was not usually determined owing to the difficulty of doing this without practically obstructing the passage of the electric current. Owing to the very considerable surface area of the coil the temperature of the solution at the cathode was only slightly higher than the temperature of the water entering the coil, several tests showed a difference of about 0.5° C. in experiments where the higher current densities were used.

Sheet iron cathodes were used. Care was taken to file them smooth, to slightly round the edges and corners, and to polish them with emery cloth. Each cathode was placed between two

sheet lead anodes of identical size, the distance between each anode and the cathode being about 0.7 cm. The cathode and anodes were held securely in place by a wooden holder.

The plating solutions were electrolyzed for one hour with a current of five amperes. The quantity of electricity passed through the solutions was determined with the aid of a watch and an ammeter.

In making a run the block-tin coil was placed in a beaker and 300 cc. of plating solution added. Water at the desired temperature was then passed through the coil until the plating solution reached practically the same temperature. The electrodes were then placed in the plating solution in the center of the coil and the electrolysis started. At the end of one hour the electrolysis was stopped and the electrodes removed from the solution. The cathode was washed with water, dried, and weighed. The increase in weight was taken as the amount of chromium deposited.

TABLE V.

30 Percent CrO_3, 0.5 Percent $Cr_2(SO_4)_3$ Solutions.

Run	Temperature ° Centigrade	Current Density Amp. per sq.dm.	Amp. Hour Yield of Chrimoum Grams
1	30	50	0.1120
2	30	75	0.1093
3	35	12.5	0.0461
4	35	25	0.0732
5	35	50	0.0937
6	35	75	0.1054
7	35	100	0.1123
30 Percent CrO_3, 1.0 Percent $Cr_2(SO_4)_3$ Solutions.			
8	35	50	0.0960
9	35	75	0.1121
10	35	100	0.1111

The deposit obtained in Run 1 was very good, in 2 badly cracked, in 3 and 4 rather dark, in 5 slightly dark, in 6, 7, and 8 light gray and very good, in 9 slightly cracked, and in 10 badly cracked. The very great effect of temperature on the yield of chromium is shown by the fact that the same yield was obtained from the 30 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution at a

temperature of 30° with a current density of 50 amperes per sq. decimeter as was obtained at a temperature of 35° with a current density of 100 amperes per sq. decimeter. Thus increasing the temperature 5° C. required a doubling of the current density in order to obtain the same yield of chromium. In view of this the

TABLE VI.

Run	Current Density Amp. per sq. dm.	Conc. CrO_3 Percent	$Cr_2(SO_4)_3$ Added Percent	Amp. Hour Yield of Chromium Grams
1	50	10	0.4	0.0928
2	50	10	0.5	0.0944
3	50	10	0.6	0.0936
4	66	10	0.4	0.1083
5	66	10	0.5	0.1117
6	66	10	0.6	0.1134
7	50	15	0.5	0.1062
8	66	15	0.5	0.1177
9	50	20	0.5	0.1109
10	50	20	0.6	0.1111
11	66	20	0.5	0.1210
12	66	20	0.6	0.1223
13	50	22	0.4	0.1128
14	50	22	0.5	0.1147
15	50	22	0.6	0.1125
16	50	22	0.7	0.1106
17	66	22	0.4	0.1213
18	66	22	0.5	0.1222
19	66	22	0.6	0.1206
20	66	22	0.7	0.1199
21	50	24	0.6	0.1103
22	5	22	0.5	0.0000
23	10	25	0.5	0.0266
24	25	25	0.5	0.0810
25	40	25	0.5	0.1054
26	100	25	0.5	0.1293

deposition of chromium was not attempted at still higher temperatures. The 30 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution was considered the better plating solution of the two, as the deposits obtained from it had a less tendency to crack. Deposits obtained from the above solution at a temperature of 35° with a current density of about 75 amperes per sq. decimeter had a much less tendency to crack than deposits obtained at a temperature of

10° with a current density of 24 amperes per sq. decimeter. The cracking of deposits of chromium on iron and on copper was found to be largely reduced by starting the deposition with a low current density and gradually increasing it to the desired value.

It was found possible to obtain deposits about 1.5 mm. thick from the 30 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution at a temperature of 35° with a current density of 75 amperes per sq. decimeter. On attempting to obtain thicker deposits, trees formed rapidly and then practically all the chromium was deposited on the trees. It is well known that the treeing of deposits is favored by a high potential gradient through the plating solution during electrolysis. Thus the tendency for deposits to tree may be reduced by making the plating solution more conducting or by the use of a lower current density.

A series of experiments were made to determine the conditions under which good yields of chromium could be obtained at lower current densities. The use of lower temperatures, which were known to permit lower current densities to be used, was not investigated at first because much better deposits had been obtained at the higher temperatures.

All the deposits obtained with a current density of 50 amperes per sq. decimeter were good, those obtained from solutions containing 20 percent CrO_3 or more were very good. All the deposits obtained with a current density of 66 amperes per sq. decimeter, except those from the 22 percent CrO_3 solutions containing 0.4 percent to 0.6 percent $Cr_2(SO_4)_3$ inclusive, were cracked. The results show that the yield of chromium increases with the concentration of chromic acid until a 22 percent CrO_3 solution is reached and then decreases, and increases with the concentration of chromic sulphate added until 0.5 percent has been added and then decreases. The 22 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution gives the best deposits and the greatest yields of chromium. It gives about the same yield of chromium with a current density of 40 amperes as the 30 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution with a current density of 75 amperes per sq. decimeter, and consequently should give considerably thicker deposits.

Experiments were made to determine whether the conductivity of the plating solutions could be decreased by the addition of alkali chromates. It was found that the conductivity was mate-

rially decreased rather than increased by the addition of alkali chromates, and in addition the yield of chromium was cut down.

Experiments were also made to determine whether the presence of dissolved chromic oxide was advantageous. It was found to be distinctly disadvantageous.

TABLE VII.

Run	Temperature ° Centigrade	Conc. CrO_3 Percent	$Cr_2(SO_4)_3$ Added Percent	Current Density Amp. per sq. dm.	Amp. Hour Yield of Chromium Grams
1	30	22	0.5	25	0.1047
2	30	22	0.5	40	0.1199
3	30	22	0.5	50	0.1256
4	25	23	0.5	15	0.0996
5	25	23	0.5	20	0.1072
6	25	23	0.5	25	0.1145
7	25	23	0.4	15	0.1028
8	25	23	0.3	15	0.1017
9	25	24	0.5	15	0.1021
10	25	24	0.4	15	0.1039
11	25	24	0.35	15	0.1045
12	25	24	0.3	15	0.1028
13	25	25	0.5	15	0.1009
14	20	23	0.35	10	0.0977
15	20	23	0.3	10	0.0988
16	20	23	0.25	10	0.0957
17	20	24	0.35	10	0.0972
18	20	24	0.3	10	0.1002
19	20	25	0.3	7.5	0.0909
20	20	25	0.3	10	0.1044
21	20	25	0.3	12.5	0.1060

Table VII shows that good yields of chromium are obtained with much lower current densities at lower temperatures. For instance, practically the same yield of chromium is obtained at a temperature of 20° with a current density of 10 amperes per sq. decimeter as is obtained at a temperature of 35° with a current density of 40 amperes per sq. decimeter. The deposits obtained at the lower temperatures and lower current densities were as good, if not better, than those obtained at a temperature of 35°.

Tests were made to determine what thickness of chromium could be deposited at the lower current densities. The cathodes,

copper plated rods, were placed in the center of cylindrically bent sheet lead anodes. The top of the anode was one centimeter below the surface of the plating solution. This allowed the solution to flow up between the electrodes and out over the top of the anode. The distance between electrodes was two centimeters. The current was increased frequently to keep the current density constant as the surface area of the cathode was increased with the deposition of chromium. The composition of the plating solution was kept constant by the addition of chromic acid solution. The temperatures of the plating solutions were kept constant to within 0.5° C. The voltage varied with the current density between 3.0 and 3.5 volts.

TABLE VIII.

Conc. CrO_3 Percent	$Cr_2(SO_4)_3$ Added Percent	Temperature ° Centigrade	Current Density Amp. per sq. dm.	Thickness of Deposit, in Cm.
30	0.5	35	75	0.15
22	0.5	30	25	0.47
24	0.35	25	15	0.7
25	0.3	20	10	1.15

Table VIII shows the results obtained in tests to determine what thickness of chromium deposit could be obtained at various current densities. By thickness of deposit is meant that thickness of chromium obtained just before the deposit began to tree badly. The results show that for plating conditions giving practically equal yields of chromium, the thickness of chromium obtained varied inversely with the current density. Thicker deposits could probably be obtained at still lower temperatures and current densities, but a deposit nearly ½ inch (1.25 cm.) thick when plated on one side only was considered thick enough for all ordinary requirements.

Some trouble was experienced with the chromic sulphate at this time. A new lot of chromic sulphate gave considerably different results than the chromic sulphate previously used. It was found to contain an excess of chromic oxide. The addition of the correct amount of sulphuric acid only partially corrected matters. A couple lots of chromic sulphate were made in the laboratory.

These chromic sulphates gave yields of chromium identical with those obtained with the old chromic sulphate only when 1/6 more of one and ⅓ more of the other were used. This is not totally unexpected behavior as there are several chromic sulphates which are ionized to different extents.

If a 22 percent CrO_3 0.5 percent $Cr_2(SO_4)_3$ solution, at a temperature of 35° C., is electrolyzed with a gradually increased cur-

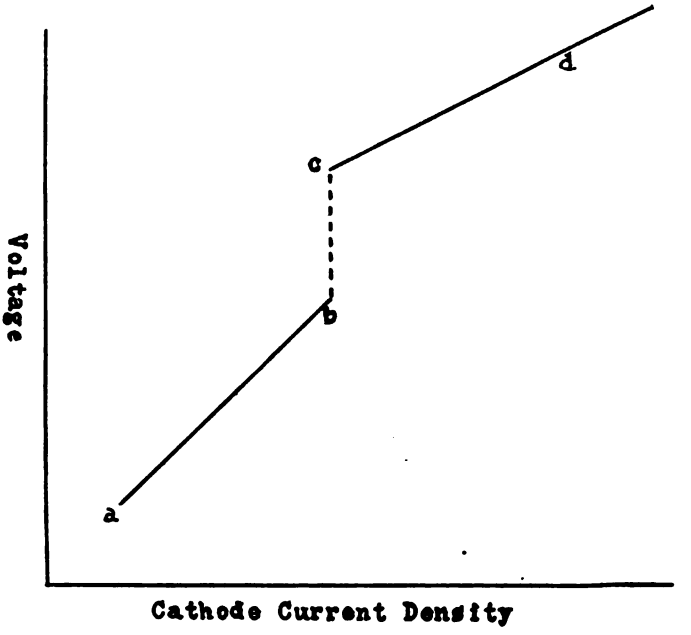

FIG. 1.

rent and a curve then plotted between the cathode current density and the voltage between the electrodes, a curve of the general type given in Fig 1 will be obtained. Most chromic acid chromic sulphate plating solutions give somewhat similar curves. Along the line *ab* only reduction takes place at the cathode. At *b* the voltage suddenly jumps to *c* and then along the line *cd* hydrogen is evolved, chromium is deposited, and chromic acid is reduced. The break in the curve results from the formation of a film on the cathode. This film is a brown substance and is probably the

"chromium chromate" observed by Geuther and others, and which has been given various formulas, CrO_2, $CrCrO_4$, $Cr_2O_3CrO_3$.

It seems possible to obtain the cathode film from almost any chromic acid solution. The formation of the film is not always attended with a noticeable increase in the voltage. The cathode film is easily dissolved by the plating solution so that if the cathode is not immediately removed from the plating solution and washed with water when the electrolysis is stopped, the film will be dissolved.

The current density at which the cathode film forms varies with the conditions and may be quite different in duplicate runs under apparently the same conditions. The duplicate run may require nearly twice the cathode current density to form the cathode film.

The nature of the cathode used has a considerable influence on the formation of the film. The film appears to form at a lower current density on a chromium cathode than on copper, iron, nickel, or graphite cathodes. A current density of about 50 amperes per sq. decimeter was required to form a film on a graphite rod from a 22 percent CrO_3, 0.5 percent $Cr_2(SO_4)_3$ solution at a temperature of 35° C. although a current density of about 10 amperes per sq. decimeter would cause the formation of a film on a chromium cathode under the same conditions. A periodic formation and dissolving of the cathode film has been observed when graphite cathodes were used.

THEORETICAL.

Chromic acid chromic sulphate plating solutions contain chromium with two different valences, 3 and 6, so there is the possibility of depositing chromium from either valence or from any other produced by reduction. It should be possible to determine the valence from which chromium is deposited by contrasting the behavior on electrolysis of solutions containing chromium with a valence of 3 and 6 with solutions containing only one of these valences.

Chromic acid chromic sulphate solutions are reduced, apparently quantitatively, with low cathode current densities. With higher current densities a film forms on the cathode and then hydrogen is evolved, chromium is deposited, and chromic acid is reduced.

Strong C. P. chromic acid solutions are reduced, apparently quantitatively, with low current densities. With higher current densities a film forms on the cathode and then hydrogen is evolved, quantitatively. With very much higher current densities chromium may be deposited and chromic acid reduced.

When chromic sulphate solutions are electrolyzed, hydrogen is evolved and chromic sulphate reduced to chromous sulphate. When a considerable amount of the chromic sulphate has been reduced, chromium is deposited.

If C. P. chromic acid solutions are electrolyzed with moderate current densities and in the presence of a cathode film, no chromium is deposited or chromic acid reduced. This behavior eliminates the possibility that the chromium deposited from chromic acid chromic sulphate solutions under similar conditions is deposited from a valence of 6 or from any other valence produced directly from this valence by reduction. Thus there is left only the possibility that the chromium is deposited from a valence of 3 or from another valence produced from this by reduction. The behavior of chromic sulphate solutions when electrolyzed indicates that chromic ions are partially reduced to chromous ions and that chromium is then deposited from both ions. A similar state of affairs seems to take place when chromic acid chromic sulphate solutions are electrolyzed. This should not be taken to mean that chromous ions are stable in strong chromic acid solutions. Chromium is deposited from chromic acid chromic sulphate solutions only when the cathode is covered with a film. The chromous ions are produced at the surface of the cathode, or under the cathode film. There seems to be good evidence that the solution at the surface of the cathode is only slightly acid at best. The cathode film is easily dissolved by chromic acid solutions. Thus the formation of the cathode film is good evidence that the solution at the surface of the cathode is practically neutral. The fact that C. P. chromic acid solutions are easily reduced in the absence of a cathode film but not in the presence of the film is additional evidence.

The theory, then, of the deposition of chromium from chromic acid chromic sulphate solutions with moderate current densities is first the formation of a film on the cathode with a nearly neutral solution in contact with the surface of the cathode. Then chromic

ions are partially reduced to chromous ions and chromium deposited from both chromic and chromous ions. Some of the chromous ions diffuse out through the film and reduce the chromic acid or attack the film itself. This accounts for the chromic acid reduced. The formation of the film with a neutral solution in contact with the surface of the cathode would seem to result from the migration of acid ions away from the cathode and from the reduction of chromic acid.

The deposition of chromium and the reduction of chromic acid when C. P. chromic acid solutions are electrolyzed with very high cathode current densities seems to be merely what would be expected from chromic acid solutions containing very small amounts of chromic ions. All chromic acid contains traces of sulphuric acid and nitric acid or sulphates and nitrates, and there is always some chromic acid reduced before the cathode film is formed. In fact the formation of the film is evidence that reduction has taken place. If a very slight amount of chromic sulphate is added to C. P. chromic acid solutions which are then electrolyzed, there will be no chromium deposited or chromic acid reduced at the cathode current density at which the cathode film forms but only at a considerably higher current density.

SUMMARY.

Very good deposits of chromium have been obtained from chromic acid solutions containing small amounts of chromic sulphate. The deposition of chromium is affected very markedly by the percent of chromic acid and chromic sulphate present and by the temperature of the solution and the cathode current density used, so that good results are obtained only by a careful control of these factors. The thickness of chromium deposits obtainable depends on the current density, the lower the current density the thicker the deposit. The use of low temperatures makes it possible to obtain fair ampere-hour yields of chromium at comparatively low current densities. A deposit ½ inch (1.25 cm.) thick has been obtained from a plating solution containing 24.5 percent CrO_3 and 0.3 percent $Cr_2(SO_4)_3$ at a temperature of 20° C. with a cathode current density of 10 amperes per sq. decimeter. A yield of 0.10 g. chromium per ampere-hour may be obtained under these conditions with a voltage of a little over 3 volts with an

electrode distance of about one inch (2.5 cm.). The 0.3 percent $Cr_2(SO_4)_3$ is a very essential constituent of the plating solution, as without it no more than traces of chromium would be obtained under the conditions given.

The color of the deposit of chromium obtained from chromic acid chromic sulphate solutions varies somewhat with the conditions, but is usually a very light gray. It has a hardness of 75 on the scleroscope and is practically unaffected by air, oxygen, or chlorine at temperatures up to 300° C. It oxidizes at about the same rate as nickel at a temperature of 1,200° C.

The theory of the deposition of chromium from chromic acid chromic sulphate solutions seems to be first the formation of a film of basic chromic chromate on the cathode with a very weak acid solution in contact with the cathode. Then there is a partial reduction of chromic ions to chromous ions and the deposition of chromium from both chromous and chromic ions together with an abundant evolution of hydrogen. The chromous ions also react with the film or with the chromic acid outside the film, causing the reduction of a considerable amount of chromic acid.

The formation of a film on the cathode is almost always accompanied with a sudden increase in the voltage between the electrodes and by the sudden evolution of hydrogen at the cathode. The film can be obtained in almost any chromic acid solution. It is a brown substance, which has been obtained by Geuther, Buff, Morges, and Carveth and Curry.

Strong C. P. chromic acid solutions are reduced practically quantitatively with low current densities in the absence of a cathode film. At higher current densities a cathode film forms and then hydrogen is evolved quantitatively. At very high current densities chromium may be deposited and chromic acid reduced.

Strong chromic acid solutions containing small amounts of chromic sulphate are reduced quantitatively with low current densities in the absence of a cathode film. At higher current densities a cathode film forms and then chromium may be deposited, chromic acid reduced, and hydrogen evolved. With very small amounts of chromic sulphate present hydrogen is evolved quantitatively at the current density at which the cathode film forms

but at higher current density chromium begins to be deposited and chromic acid reduced.

When lead anodes are used practically all the chromic acid reduced at the cathode is oxidized back to chromic acid at the anode. This makes it possible to maintain the composition of the plating solution desired for an indefinite length of time.

The use of ferro-chromium anodes as a cheap source of chromium for plating or refining is impracticable owing to the lack of a process for removing the iron periodically from the plating solution without adding an equally objectionable substance.

Chromium plating has commercial possibilities owing to its extreme resistance to corrosion by air, moisture, and many chemicals.

The above work was carried out under the direction of Professor W. D. Bancroft, to whom the writer wishes to express his appreciation for the kindly criticism and many suggestions. The latter part of the work was carried on through the financial assistance of Dr. H. R. Carveth, of the Niagara Electrochemical Co.

DISCUSSION.

F. S. WEISER[1]: I would like to ask if you can give us any information as to the physical characteristics of that deposit of chromium? How would it act under heating? Was it brittle? Did it seem to be formed in layers, or did it seem to be a good, solid, coherent deposit?

W. D. BANCROFT[2]: It is a pretty good, solid deposit, as I remember it. It was a long time ago; what we had hoped to do was to plate on iron and then heat in hydrogen and get a chrome steel surface. Nickel goes into iron pretty fairly readily; but chromium does not alloy with iron until you get up to 1,200° C., which is too near the melting point to be safe. That was the reason we dropped the thing. As I remember it, the deposit is not very brittle and is fairly hard, but of course it is not anything like as hard as chromium carbide.

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[2] Prof. of Physical Chemistry, Cornell University.

F. N. SPELLER[3]: Several years ago our Research Laboratory investigated the embrittling effect of pickling of pipe, with results which confirm those of the authors of this paper. We found that the most practical method of removing the brittleness in pipe after pickling was to heat under water to about 190° F. for two or three hours prior to galvanizing: this has been our practice since 1913. Where the pipe is used for signal connections or similar purposes it is important to see that the metal is heated for sufficient time under proper conditions to remove this brittleness. Otherwise it may be in a dangerous condition for use and is liable to cause a failure at the threads.

[3] Metallurgical Engineer, National Tube Co,, Pittsburgh, Pa.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

FUNDAMENTAL PROBLEMS IN ALLOYS RESEARCH.[1]

By H. E. Howe.[2]

ABSTRACT.

A statement of the fundamental investigations which should be undertaken to enlarge our knowledge of metallic alloys, particularly of the basic physical and chemical data which should be known in order to handle alloys and related substances intelligently. As representing the Alloys Research Association work of the National Research Council, the author states that the work of this branch will be at first to supply needed information, where it already exists, and later to incite laboratories to undertake the determination of unknown but necessary and desirable data.—[J. W. R.]

Notwithstanding the remarkable achievements that have followed research in the field of alloys, both ferrous and non-ferrous, it is apparent to those who are engaged in the production and use of alloys that we have scarcely more than begun upon the solution of the numerous large problems. It seems necessary to emphasize that there is far more to be done than has been done, because only recently one manufacturer of alloys remarked that it is hardly necessary for the consumer to concern himself with research looking toward new products, since all that is necessary is for him to make his wants known to this producer and the new metal will be provided. In contrast to this there are many manufacturers who realize that they cannot hope to greatly improve their present products until more is known of the principles which underlie the processes employed, and until data with respect to properties of the constituent metals have been completed. When

[1] Manuscript received March 6, 1920.

[2] Chairman, Division of Research Extension, National Research Council.

as a result of research we learn what takes place in an alloy when it undergoes various treatments to which it is subjected, then we shall be better able to find ways to control these changes and so give us results desired to meet specifications.

It must be understood that a science is necessary in any industrial field before it can be efficiently applied and research strives to build up this science. It is difficult to draw a sharp line which can be considered the boundary of fundamental research, but for the purposes of this discussion, let us define it as work undertaken to establish facts that will extend the boundaries of our knowledge, quite apart from the immediate commercial application of the results obtained.

It is not intended to depreciate a great deal of development work now being done in many laboratories, which is closely related to fundamental research but which is nevertheless more nearly the solution of works and production problems. Industrial laboratories frequently contribute information upon fundamental problems, but as a rule such information originates in the laboratories of educational institutions, those supported co-operatively through associations, and the government laboratories.

I wish to point out how incumbent it is upon us all to support fundamental research, and to indicate some of the problems which are awaiting solution. Some producers and consumers have emulated the jelly-fish in their attitude toward fundamental research, and have obtained their nourishment by simple absorption from the stream in which they float. As one after another of the problems have been met which cannot be solved in the light of our present information, it has dawned upon the producer and the consumer alike that we must maintain an uninterrupted stream of fundamental information, and we therefore see an increasing willingness to pool resources for necessary work.

Research rests upon information as its starting point, and its product is likewise information. In order to complete the published data on standard alloys, giving their uses, composition, tolerance in composition, physical properties, variance with differences in composition and with impurities, a good deal of investigation is required. Such a list should cover sand and chill casting, die casting, rolling, forging, extrusion, and should include not only the ordinary tests but more extensive data. The follow-

ing characteristics in particular should be determined: tensile strength, elongation, yield point, modulus of elasticity, specific gravity, compressive strength, impact resistance, impact fatigue, Brinnell hardness, scleroscope hardness, melting point, pouring temperature, pattern shrinkage, effect of temperature on the mechanical properties, thermal conductivity, electrical resistivity, micro-structure, and chemical characteristics. Many of these tests should be conducted at different temperatures. Other constants are the critical point, specific heat, latent heat of fusion, latent heat of vaporization, and thermal conductivity and expansion. The entire group of electrical and magnetic properties are important in many cases, while solubility, susceptibility to attack by acids and alkalies, porosity of metals, effect of outside agencies, such as pressure and magnetic field, must be included.

A similar listing and testing of the non-standard alloys should be undertaken, the primary purpose being to determine whether they may not become standards themselves, or acceptable substitutes for present standards to be employed when prices make that advantageous, or as the now rare elements become commercially available. It is recognized that various attempts have been made from time to time to compile tables giving the physical and chemical properties and compositions of commercial alloys, but the work has never been completed, and surely anyone in the industry will welcome authoritative information of this kind. Much of the work that has been done in determining these constants has unfortunately been on samples whose complete history is not known, and the results must therefore be checked.

The corrosion problem is a very large one, and we have much ahead of us in determining the nature of corrosion as well as in developing methods for its study. We need a comprehensive study of exposure tests made upon such metals as zinc, copper, brass, nickel, aluminum, steel, tin, and their alloys, to determine the rate and character of corrosion under moist atmospheric conditions, by sea air, and similar more or less common conditions which structural metals are called upon to resist.

We have yet to develop a high-silicon iron or other alloy which is sufficiently non-corrosive to answer the requirements of the chemical industry, and yet which possesses a satisfactory degree of machinability. Of course, such an alloy should be inexpensive.

Comparative metal technology offers an attractive field for research and would include a careful comparison of mechanical properties, as well as general physical and chemical characteristics. It is therefore closely related to the determination of the physical and chemical constants mentioned earlier. Another field which promises much is the study of the effect of traces, or small percentages of elements usually regarded as impurities, upon the properties of metals. We are already familiar with what has been made possible by the use of comparatively small percentages of certain elements in alloys, and yet the large number of combinations possible would seem to offer a prize attractive to some of our best talent.

Our information on the properties of pure metals is really fragmentary. The phase rule diagram has been nearly completely worked out with respect to certain pairs of metals, but many important pairs have not been adequately studied. When we come to three component systems scarcely anything has been done, and in modern practice the number of elements present is more likely to exceed than be below three in number.

There seems reason to believe that the occluded gases in metals may have a more serious effect than some of the impurities which we take pains to eliminate, and as a result of more liberal allowances of phosphorus and sulphur during the war, a series of investigations is now under way with respect to the effect of these elements upon iron, with the hope that standard specifications can be drawn in the light of the new information. The effect of solid and gaseous impurities and methods for their elimination offers a most interesting field.

A study of deoxidizers and fluxes for non-ferrous metals has been urged. This subject has had more attention in the iron and steel field than in non-ferrous alloys. The effect of melting practice upon slag inclusions, including a comparison of the amounts of these inclusions in electric furnace and crucible products, is suggested for investigation.

Other problems suggest themselves when special applications of metals are considered. Die casting is really in its infancy, and when aluminum alloys are cast in this manner, what are the effects of impurities in them; what metal or metals can be added to molten aluminum or its alloys to counteract the detrimental effects

of such impurities; what is the best aluminum flux; what are the elastic limits of aluminum alloys at temperatures ranging from 600° to 1,000° F. (315°–540° C.); what gray iron composition will best withstand the action of molten aluminum and its alloys; what amount of reduction should metals undergo in order to have the best physical properties?

A comprehensive study of pouring temperatures is much to be desired, as well as the effect of the nature of the furnace atmosphere in metallurgical processes. The whole subject of heat treatment, including the change of properties which is possible, the causes of deformation in tempering and annealing, and other heat treatment, the determination of the factors affecting decarburization in the annealing process, and in general a comprehensive research on heat treatment factors.

Accurate data are urgently needed on the specific heats at ordinary and higher temperatures of metallurgical compounds and such materials as sulphides, oxides, chlorides, sulphates, and carbonates. This information would be of the greatest value in calculating blast furnace charges and in calculating the equilibria in metallurgical-chemical reactions. Thus, if we knew accurately the specific heats of ferrous sulphate, ferric sulphate, copper sulphate, the oxides of iron and copper, and of sulphur trioxide, we might expect to calculate with reasonable accuracy the equilibria which obtain in the metallurgical reaction known as sulphatizing roasting. There are a number of such metallurgical reactions which could thus be accurately studied, and a value difficult to compute would be derived by the metallurgical industries from the use of such data, which can only be obtained through research.

We cannot expect to enumerate all of the problems which invite the attention of those qualified to conduct research. We should not pass on, however, before mentioning the great need for more accurate and rapid methods of testing, of making analyses, producing photomicrographs, etc. To devise such methods usually calls for extensive research, much of which borders upon the fundamental. A reliable test for machinability is much needed. We would like to know how to determine the relative efficiencies and life of various bearing metals, and testing methods which can be applied without destroying the article under test would be of enormous help. Something has been started in this direction by the

use of X-rays in examining metals and through the study of crystal growth and structure in alloys of known composition at various stages of fatigue. We still have to develop a test which will truly indicate the malleability and shock-resisting qualities of malleableized cast iron.

The methods of working applied to different metals and the effect upon them is yet another field. For example, what is the influence of forging methods on the fibre of the product? Oftentimes material of the correct chemical composition fails after being subjected to certain forging methods. What are the causes of the embrittling effect of galvanizing and tinning upon malleable iron, and why do pin-holes tend to form in the surface of malleableized castings of medium and heavy sections in conjunction with low carbon? What are the methods for correction? It may be possible that different types of furnaces should be employed for different alloys, but in the present state of our information we cannot prescribe the best conditions for the most effective work.

It is, of course, apparent that from the very nature of the work to be done, no one organization can either hope or be expected to perform the work as thoroughly as is needed. The data sought are frequently difficult to obtain and involve a long-time study. And yet we must have the information. In other countries steps are being taken to carry on this work co-operatively and much study has already been given to the possibilities here in America.

Since the problems are fundamental, they are only indirectly connected with the works problems in any particular industry, and it seems therefore that alloys present an opportunity for co-operation. We can unite our efforts upon work of this kind and still leave for the individual laboratories the application of the fundamental data obtained in their own particular work. We recognize that in order to have research become the factor it should in any industry, that industry should make its research laboratory an intimate part of its own organization. This can be done to even better advantage if some of the problems common to all can be assigned to laboratories equipped especially for their solution, leaving the attention of the staff in any particular industrial plant to concentrate upon the type of problem which cannot be so well studied elsewhere.

With this in mind, the National Research Council has undertaken the formation of an Alloys Research Association which will devote its efforts initially to an informational service, believing that the greatest opportunity for immediate service lies in that direction, and that the questions to be answered will very soon emphasize to those supporting such service the necessity of extending their efforts to research itself. It is to be hoped that extensive fundamental research can go forward in any laboratories prepared to undertake it, and that the informational service, acting as a clearing-house, can make this work more effective than it otherwise would be. There is no doubt that fundamental science offers an ideal field for the most that is possible in co-operation, and the American Electrochemical Society is cordially invited to support the project.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

STELLITE.[1]

By Elwood Haynes.[2]

Abstract.

An account of the invention of Stellite and its varieties; its manufacture by melting together the constituent metals, or by simultaneous reduction of a mixture of the oxides of these metals by carbon or aluminum, in crucibles or in the electric furnace. Account is also given of the properties and performances of the alloy. [J. W. R.]

Realizing many years ago that an alloy that would take a cutting edge and at the same time resist the action of the atmosphere would fill a long-felt want, I made attempts even then to produce such a mixture or combination of metals. I found, however, that the problem was beset with many difficulties. Alloys containing copper were always subject to the tarnishing action of moist air and sulphuretted hydrogen; mixtures containing nickel and copper only possess the same disadvantages, though to a limited degree. Aluminum alloys with copper and nickel gave considerable hardness and a very high elastic limit, but they would tarnish in moist air, particularly in the presence of hydrogen sulphide.

In 1891 I made an alloy of nickel and tungsten, and, while this was not immune to acids, it resisted atmospheric influences remarkably well. This alloy was made by melting pure tungsten and pure nickel in a small crucible composed of a mixture of pure alumina and pure magnesia. The fusion was made in a small furnace of my own construction. The fuel used was natural gas, using air blast from a small foot-bellows.

[1] Manuscript received March 15, 1920.

[2] President, The Haynes Stellite Co., Kokomo, Indiana.

Later, in 1898, I produced pure alloys of nickel and chromium by the reduction of their mixed oxides with pure aluminum. The alloy of nickel and chromium thus formed took a high polish, and retained its luster in boiling nitric acid when the chromium constituted more than twelve to fifteen percent of the alloy. This alloy could be filed rather readily, and could be worked cold into rods and sheets if sufficient care was exercised.

I next produced an alloy of cobalt with chromium in the same manner, but when the reaction took place a certain amount of free oxygen was evolved, and the metal was thrown from the crucible. This was due to the fact that the higher oxide of cobalt (Co_2O_3) was used, while in the former experiment NiO was employed.

The reaction for the production of the nickel alloy was as follows:

$$3NiO + Cr_2O_3 + 2Al_2 = Ni_3Cr_2 + 2Al_2O_3.$$

The reaction in the case of cobalt was:

$$2Co_2O_3 + Cr_2O_3 + 3Al_2 = Co_4Cr_2 + 3Al_2O_3.$$

It is obvious that by varying the proportions of the various oxides, alloys of varying compositions can be obtained.

It was only a step from this reaction to the production of the alloy by the simultaneous reduction of the oxides of their constituent metals by means of carbon.

Afterwards, they were produced on a commercial scale by melting pure nickel or pure cobalt with chromium. Since the cobalt-chromium alloys possessed great hardness and could be worked at a bright red heat, it seemed to be the more promising field for further investigation, and when, in the early part of 1900, large quantities of cobalt ore were discovered in Canada, and it became possible to procure the cobalt oxide at a comparatively reasonable price, I decided to place the alloy on a commercial basis.

The discovery of these alloys was first made public at a meeting of the American Chemical Society, in San Francisco, in 1910.

About this time I discovered that by adding tungsten or molybdenum to the cobalt-chromium alloy its hardness could be very much increased, though the addition of either of these metals in any considerable quantity rendered the alloy unworkable either

hot or cold. It could, however, be cast into almost any desired form, and when cast bars were ground to a cutting edge and placed in the tool-holder of a lathe, the alloy at once showed a considerable advantage over high-speed steel as a lathe tool.

The first remarkable test of this sort was made in the machine shop of the Haynes Automobile Company. A large boring mill had been purchased for boring cylinders. This mill was supplied with a boring head in which were inserted small radial cutters which bored out the interior of the cylinders directly from the rough castings. I was informed by our superintendent that he had found it impossible to work the mill to more than half its rated capacity on account of "burning" the steel tools. We had up to that time made only a few tests on the lathe of Stellite tools, but he was very anxious to try the alloy in the form of boring cutters. I accordingly produced a set of cutters of Stellite, which were inserted into the boring head. When I came to the factory the next day, about 11.30 in the forenoon, I asked the man at the mill what success he had achieved, and he replied that he "had a day's work out at twenty minutes of eleven in the forenoon." In fact, he was boring more than twice as many cylinders in a day with Stellite tools as could possibly be bored with steel ones. This test fully demonstrated the practical utility of Stellite tools.

In 1912, another paper was read on this alloy in New York, at one of the sessions of the International Congress of Applied Chemistry.

It was found quite difficult to make metal of uniform texture and quality in the form of castings, but most of the difficulties have been overcome, and we are now placing upon the market cast tools of various kinds made of Stellite, which are of standard quality both as to strength and hardness.

The alloys are made almost entirely in electric furnaces of the Snyder type. The materials composing the alloy are placed in the furnace in the usual manner, and the current turned on. The alloy fuses rapidly, without much oxidation, under the intense heat of the electric arc. We find that of the metals composing the alloy, chromium is most readily oxidized, while cobalt seems to show more volatilization, and tungsten is subject to the least change. It is true that the portion of furnace above the metal becomes filled with nearly pure carbon monoxide. This gas will

oxidize chromium under certain circumstances at very high temperatures, though apparently no free carbon is produced in the furnace. This is probably because there is sufficient free oxygen or carbon dioxide to re-oxidize any carbon that may be temporarily produced.

At first much difficulty was experienced with the electric furnace linings, but after a certain amount of experimental work we were able to produce a magnesite lining which gives most excellent satisfaction in practice. When we first began the use of these furnaces, we considered ourselves fortunate if we could get eight or ten melts without either complete re-lining or heavy repairs. We now commonly obtain from two thousand to three thousand melts from a single lining, and some of them stand even higher than this.

The electric arc, on account of its extremely high temperature, causes a certain amount of volatilization or oxidation in the melting of many metals, but Stellite withstands the conditions remarkably well, particularly after the fusion is once made. In melting scrap, however, if certain precautions are observed only a very slight loss is experienced in re-melting. Stellite can be melted in covered crucibles under suitable precautions with a loss of less than two percent, and sometimes it does not even reach one percent.

Not only have the Stellite alloys containing cobalt, chromium, and tungsten, or cobalt, chromium, and molybdenum shown great economic advantage as lathe tools, but the binary alloys (consisting of cobalt and chromium only) have likewise received a wide application in the form of dental instruments, surgical instruments, pocket knives, etc.

A modified Stellite alloy, known as Festel metal, consisting of cobalt, iron, and chromium, is also manufactured into table knives, which give excellent results in service.

All of the above alloys are practically immune to all atmospheric conditions, whether the air be moist or dry, or whether it contain minute quantities of sodium chloride or sulphuretted hydrogen. Knives made of this alloy can be used for cutting all sorts of fruit, including lemons, oranges, apples, etc., without becoming discolored in the slightest degree. A new and interesting application of malleable Stellite is as a substitute for gold in

the manufacture of pen points for fountain pens. The tips of these pens may, if desired, be made of extremely hard Stellite, which can be welded to the malleable alloy. This application is particularly gratifying because the metals replaced, gold and iridosmium, are exceedingly expensive.

DISCUSSION.

J. W. RICHARDS[1]: During the war Mr. Haynes devoted the larger part of his production to surgical instruments. This metal is splendid for that use, being non-corroding, very hard and keeping a very fine edge. This pocket knife will illustrate its use for surgical instruments; it was given me by Mr. Haynes. Medical men say that stellite is an ideal material for surgical instruments, and it played a large part during the war in the equipment of our army and navy.

S. A. TUCKER[2]: I think that one thing that is a drawback in the production of this material is the price; they charge $7.00 each for these knives.

COLIN G. FINK[3]: I would like to emphasize one of the main points in Mr. Haynes's paper, and that is this: Mr. Haynes has been trying to make this high melting cobalt alloy, stellite, in gas-fired and other fuel furnaces and could not get a uniform product. The electric furnace was tried and the product was absolutely uniform and could be easily controlled. It is another case where the electric furnace has won out over the old gas-fired and blast furnaces. As Professor Richards acknowledges, this is not a case for the blast furnace.

J. W. RICHARDS: It is interesting to note that chromium is so oxidizable that it cannot be melted in the ordinary open-hearth furnace. Armor-plate steel, containing three or four percent of chromium, is cast into ingots, but about 50 percent of it has to be returned to be remelted. In remelting it in open-hearth furnaces, the whole of the chromium is lost; it goes into slag. It is a great

[1] Prof. of Metallurgy, Lehigh University.
[2] Chemical Foundation, New York City.
[3] Head of Laboratories, Chile Exploration Co., New York City.

waste of our chromium resources to think that 50 percent of the chromium put into the making of chromium steel is lost in remelting the scrap. In England they are now using the electric furnace to remelt this armor-plate scrap, simply because they are compelled to save the chromium.

The reason the knives cost so much is that the metal is not forgeable; the blades are cast into shape and then ground smooth. Their manufacture is a costly operation.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 9, 1920, President Bancroft in the Chair.

SOME ELECTRICAL PROPERTIES OF TITANIUM ALLOYS.[1]

By M. A. HUNTER AND J. W. BACON.[2]

ABSTRACT.

Describes the production of pure titanium by reduction of titanium tetrachloride by sodium. Some of its physical and chemical properties are given. Tests were then made with this material, alloying it with Norway iron; magnetization and hysteresis tests were made on the products, showing higher magnetization curves and lower hysteresis losses. Silicon-iron thus treated gave exceedingly high permeability and low hysteresis loss. Alloys were also made with nickel, copper, nickel-iron and nickel-copper. The alloys were made into wire and their electrical resistivities measured. Additions of Ti up to 5 percent increased the resistance moderately, but the wires oxidized badly when run at a red heat.

[J. W. R.]

The production of metallic titanium is probably one of the most difficult of metallurgical processes. Within recent years, however, various alloys of titanium have been produced. These alloys may be divided into two distinct classes. In the first class we have those alloys which are produced by the use of aluminum or silicon. These alloys contain in general a high percentage of free titanium, but associated with this there is always to be found a considerable amount of the aluminum or silicon which is used for reduction. In the second class we have those alloys which are produced by the use of carbon. Here, however, the affinity of carbon for titanium is so great that only under exceptional circumstances do we find any of the titanium in the resulting alloy in the free

[1] Manuscript received March 8, 1920.

[2] Rensselaer Polytechnic Institute, Troy, N. Y.

metallic state. Ordinarily the titanium is present as titanium carbide.

With these two series of alloys available as sources of supply, it was a matter of considerable difficulty to determine the specific action of titanium in any investigation. In the case of the aluminum-reduced alloy, the presence of metallic impurities other than titanium masked and often completely obscured the effect of the presence of titanium: while in the case of the carbon-reduced material, it is clear that since no free titanium is present in the metal, any effects produced are not to be attributed to the effect of titanium.

However, this situation is completely changed through the introduction of a method for producing pure metallic titanium.[8] The reduction of pure titanium tetrachloride with sodium in a closed iron receptacle gives us a supply of metal which is entirely free from sodium or iron or any other impurity. The heat of the reaction is, in general, sufficient to melt the reduced titanium. The resulting product is, therefore, obtained for the most part as an aggregate of irregular beads. This material can be alloyed without difficulty with iron or any other metal. The production of this pure titanium metal has rendered possible a series of investigations on the specific action of titanium.

TITANIUM METAL.

The beads of metal do not differ in outward appearance from polished steel. They are hard and brittle when cold, but at a low red heat they may be readily forged into small rods. Attempts at drawing these rods to wire were not successful. The melting point of the metal is 1800° C. The specific gravity was found to be 4.50. This value is the mean of four determinations on various samples, ranging from small rounded grains of the size of No. 4 shot (4.53) to forged rods (4.46).

With this material two series of investigations have been carried out. The first deals with the effect of titanium on the magnetic properties of iron: the second with the electrical resistances of various titanium alloys.

[8] J. Amer. Chem. Soc. (1910), 32, 330.
Rensa. Poly. Inst. Eng. & Sci. Series, No. 1.

A. THE EFFECT OF TITANIUM ON THE MAGNETIC PROPERTIES OF IRON.

With regard to the magnetic properties of iron it may be said that the magnetic quality is a direct function of the purity of the iron. Electrolytic iron[4] is therefore a better magnetic material than other grades of iron which contain a greater percentage of impurities. This statement must however be modified in the case of alloys of iron with silicon,[5] aluminum,[5] arsenic,[6] antimony[6] and tin.[6] The addition of these materials seems to exert a specific action which is altogether apart from the improvement to be expected from the mere purification of the iron by the addition. With this in view it seemed desirable to add titanium to iron to determine whether any specific improvement can thereby be obtained.

Preparation of Materials.

Commercial Norway iron was taken in all cases as the starting material. To this, varying amounts of titanium were added. The alloys were melted in alumina crucibles in a vacuum in the Arsem furnace. The melting together of the materials was always accompanied by a considerable evolution of heat. On subsequent analysis the alloy was found to contain much less titanium than the amount added. This confirms the statement so often made that it is a difficult matter to keep titanium in the metallic state in an alloy of iron.

The following series of alloys were made:

(1) Pure metallic titanium added to Norway iron.

Sample	Ti Added Percent	Ti Found Percent	Magnetization Curve
15A	0.5	0.0065	Curve A, Plate 1
8A	1.0	0.200	" C, " 1
9A	5.0	0.285	" B, " 1

(2) Titanium alloy added to Norway iron.

The alloy added in this case was a commercial ferro-titanium produced by the use of aluminum, by the Titanium Alloys Mfg. Co. of Niagara Falls.

[4] Yensen, Univ. of Ill. Bull. No. 72.
[5] Barrett, Brown & Hadfield Trans. Roy. Dublin Soc., VII, (2), Jan., 1900. Yensen, Univ. of Ill. Bull. No. 83.
[6] Burgess & Aston. Electrochem. Met. Ind., Sept., 1909.

Sample	Ti Added Percent	Ti Found Percent	Magnetization Curve
2A	0.5	None	Curve B (Approx.)
3A	1.0	0.023	" C "

(3) Titanium alloy added to Norway iron.

The alloy added in this case was a commercial alloy of ferro-titanium produced by the use of aluminum by the Goldschmidt Co.

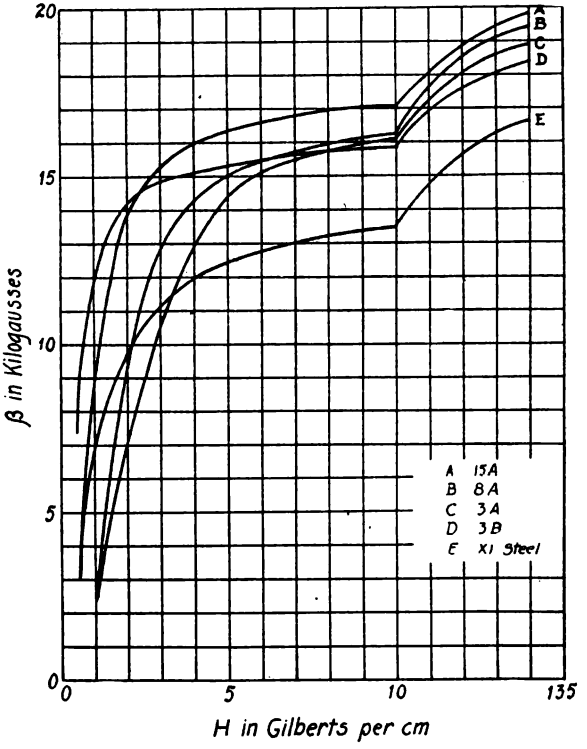

PLATE 1.

Sample	Ti Added Percent	Ti Found Percent	Magnetization Curve
10A	0.5	0.400	Curve C (Approx.)

These alloys were forged into rods and measured on the Du Bois magnetic balance. Subsequently, through the courtesy of Mr. W. E. Ruder, of the General Electric Co., the rods were

checked up by the Burrows method. The following figures are taken from the magnetization curves thus obtained.

Sample	Maximum μ	B at Maximum μ	B for $H = 100$	H for $B = 14{,}000$	Specific Resistance
2A	7,120	9,000	19,100	2.64	13.59
3A	4,300	9,000	18,725	4.24	13.61
8A	4,400	10,500	18,350	4.12	14.03
9A	4,510	10,500	19,300	4.05	19.45
10A	2,925	11,000	19,200	5.90	14.22
15A	8,475	9,000	19,400	2.08	12.99
4.5% Si. iron..	9,300	5,500	16,400	16.50	71.61

The titanium-treated alloys were annealed before measurement at 1100° C.; the silicon alloy at 780° C.

It is evident that the Norway iron treated with a small quantity of titanium (and from which practically all the titanium is subsequently removed) gives a higher magnetization curve than that obtained from any other sample. Sample 2A contains less titanium than 15A, but has probably taken up some other impurity from the commercial ferro-titanium used. The results show in general that the presence of more than a trace of titanium brings about a lowering in the magnetization curve.

On the accompanying sheet (Plate 2) comparative curves are plotted for various materials. The titanium-iron curve is from 15A. The curve for electrolytic iron is from Yensen's results. The remaining curves are for silicon-steel and standard transformer iron.

Hysteresis Losses in Titanium Treated Iron.

For hysteresis measurements commercial Norway iron was treated with small additions of pure titanium metal. For purposes of comparison a sample of the commercial iron was run through, following the same procedure as in the titanium-treated samples. The samples were forged and machined in the shape of flat rings. The hysteresis losses were subsequently measured by the Rowland method. The results obtained were as follows, the hysteresis losses being given in joules per pound per cycle:

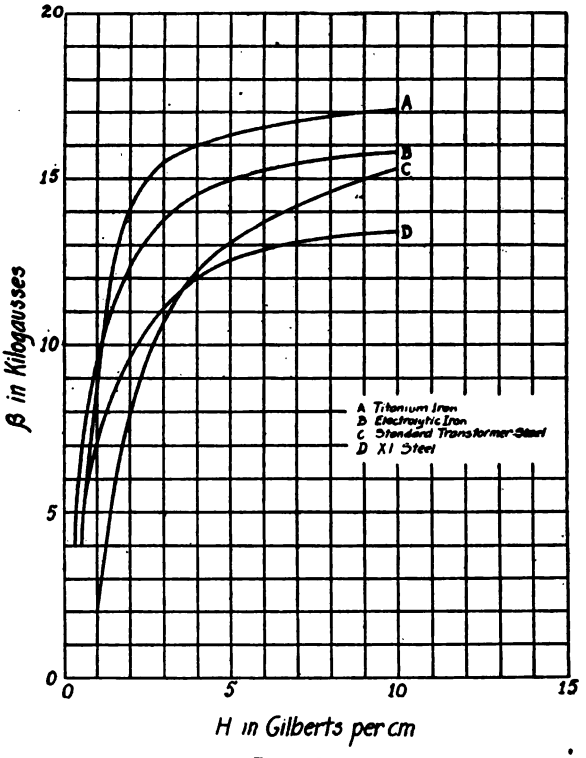

PLATE 2.

Sample	Ti Added Percent	Ti Found Percent	Hysteresis Losses at 10,000 B		Hysteresis Loss at at 15,000 B Annealed at 800°
			Annealed at 800°	Annealed at 1,000°	
1B	None	None	.....	0.00785	0.0302
3B	0.1	None	.....	0.00684	0.0243
6B	0.1	None	0.0120	0.00622	0.0278
7B	0.1	None	0.0108	0.00551	0.0252
5B	0.5	0.165	0.0189	0.01487	0.0451
4B	0.5	0.345	0.0197	0.02369	0.0551
2B	1.0	0.570	0.0229	0.02615	0.0593

It is evident from these results that the addition of a small quantity of titanium, which is subsequently removed (as in the case of 3B, 6B, 7B) improves the hysteresis loss in a sample of Norway iron (1B). If all the titanium is not removed from the

metal, the hysteresis loss increases in proportion to the amount of titanium which remains.

Ageing of the Samples.

Rings 1B and 3B were measured two years later through the courtesy of the Westinghouse Company. The results obtained give the following as compared with the earlier figures.

Sample	Area of Hysteresis Loop		Ageing in Percent of Initial Value
	Initial B. H. Units	2 Years Later B. H. Units	
1B	17,080	22,120	29
3B	14,830	18,300	23

No satisfactory tests on forced ageing have been carried out. The results however show that both pure iron and titanium-treated iron are subject to very considerable ageing.

Titanium in Silicon-Iron.

To determine the effect of titanium treatment on a silicon-iron alloy, the following samples were made by adding to an XI steel containing 4.5 percent silicon, a known quantity of commercial Norway iron together with a small amount of a 10 percent alloy of titanium in iron.

Ring 11B contained 2.00 percent Si and was treated with 0.1 percent Ti
Ring 12B contained 1.25 percent Si and was treated with 0.1 percent Ti
Ring 13B contained 1.00 percent Si and was treated with 0.1 percent Ti

Magnetization Curves of Iron-Silicon Alloys.

From the magnetization curves of iron-silicon alloys, treated with titanium the following values are taken. For purposes of comparison the values for the pure iron and titanium-treated iron are included.

Material	Maximum μ	B at Maximum μ	B for $H = 100$	H for $B = 14{,}000$
1B	13,200	10,000	18,300	1.9
3B	15,300	10,000	18,200	1.8
11B	18,900	7,500	.....	2.1
11B*	17,400	9,000	17,200	2.9
12B*	9,300	10,000	17,500	3.2
13B*	9,900	9,200	17,500	3.2

The values marked with an asterisk for 11B, 12B, and 13B were from curves determined after the sample had aged for two years.

Hysteresis Loss in Joules Per Pound Per Cycle.

Material	Annealed 800° C.	Annealed 1,000° C.	After Ageing for 2 Years
11B	0.00967	0.00479	0.00541
12B	0.0134	0.00806	0.00908
13B	0.0135	0.00755	0.00866

The hysteresis loss in these samples was quite low, though not materially lower than in the samples of titanium-treated iron which contained no silicon.

B. THE ELECTRICAL RESISTANCES OF SOME TITANIUM ALLOYS.

Pure titanium was obtained in the form of a rod by working at a red heat. A specific resistance of 88 microhm-cm. was obtained for this material. This value would appear at first sight to be inordinately high.

Several series of alloys have been made with titanium to determine its effect on the electrical resistance of various metals.

1. Nickel-Titanium Alloys.

Composition		Sp. Resistance in Microhm-cm.	Temp. Coeff.	Remarks
Ni	Ti			
90	10	66.6	.....	Very Hard
95	5	53.5	0.00077	Easily Ductile
98	2	30.3	0.00172	" "
98	2	24.7	0.0019	" "

These wires when heated to a bright red heat by an electric current oxidize to a considerable degree. When the wire is cooled the oxide splits off the wire very easily and leaves a fresh surface for further oxidation. This renders the material quite useless as a resistance wire at high temperatures.

2. Nickel-Iron-Titanium Alloys.

The combination nickel 60, iron 20, titanium 20 gave an unsatisfactory alloy. The material was brittle and could not be drawn.

An alloy containing nickel 60, iron 27, titanium 13 could be rolled sufficiently to round off the edges. On further rolling the alloy cracked badly and the operation was discontinued. An alloy containing nickel 80, iron 10, titanium 10 was also hard and brittle. No resistance metal can be expected from these combinations.

3. Copper-Titanium Alloys.

Copper and titanium combine readily to form an easily workable series of alloys. Difficulty was experienced in working these alloys when the concentration of titanium was greater than 10 percent.

Composition		Sp. Resistance in Microhm-cm.	Temp. Coeff.	Remarks
Cu	Ti			
99	1	22,38	0.000292	
98	2	35.51	0.00214	
95	5	57.2	0.	Difficult to draw
90	10			Could not be drawn

The 5 percent alloy furnished a wire which on being held at a low red heat for 15 minutes oxidized and rapidly deteriorated.

4. Copper-Nickel-Titanium Alloys.

Copper and nickel form with each other a continuous series of solid solutions giving alloys of moderately high resistance. The addition of titanium produced the following results:

Composition			Sp. Resistance in Microhm -cm.	
Cu	Ni	Ti		
83	16	1	23.	
57	41	2	52.5	
73	22	3	31.5	
48.5	48.5	3	53.3	
34	63	3	63.2	Temp. coeff., 0.000267
24	73	3	61.7	
56	40	4	51.7	
41	55	4	58.7	
24	71	5	60.3	

The addition of titanium up to 5 percent (the largest addition possible without destroying the ductility of the wire) does not materially increase the resistance of a copper-nickel alloy. Further the wires cannot be run at high temperatures by reason of their excessive oxidation.

The use of titanium in resistance wires would seem to be of little advantage. In the melting together of the materials the solution of the titanium is always accompanied by a great evolution of heat, indicating that a chemical combination is taking place. Now since these intermetallic combinations are invariably brittle, it could be foreseen that these alloys would be materially harder than an alloy in which no such combination is present. This is, indeed, borne out by experiment. When the titanium content rises above 5 percent the resulting alloy is so hard that it cannot be readily drawn to wire. Alloys with less than 5 percent of titanium have in general only moderately high resistances, and when run at a red heat deteriorate rapidly through oxidation.

SUMMARY.

1. The addition of titanium to iron improves the magnetic quality of the iron. The magnetization curves are invariably higher and the hysteresis losses lower than in an untreated specimen.

2. The action is attributed to a cleansing of the material by the addition of titanium. If additions are made in such amounts that titanium is left in the iron, the material improvement is no longer apparent. The samples will under these conditions be lower in magnetic quality than the original iron.

3. Good results were obtained by treating silicon-iron with titanium. These alloys gave an exceedingly high permeability and low hysteresis loss.

4. The ageing of the titanium-treated specimens was of the order of that of iron, though somewhat less in degree.

5. Alloys of titanium with nickel, copper, nickel-iron and nickel-copper were made. The specific resistances of these materials are only moderately high for additions of titanium up to 5 percent. Beyond this point the alloys are exceedingly hard to

draw. Such wires as were made can be run continuously only at low temperatures by reason of their tendency to oxidation when run at a red heat.

Rensselaer Polytechnic Institute,
Troy, N. Y., March 2, 1920.

DISCUSSION.

T. D. YENSEN[1]: I should like to make a correction in connection with this paper. On page 515 a reference is made to the results of my investigations of the magnetic properties of electrolytic iron, and a B-H curve is shown on page 516 (curve B). This curve was evidently plotted from the first data obtained by me on electrolytic iron.[2]

Later investigations gave much better results[3], and if the latter were used for the sake of comparison, it would be seen that the electrolytic iron is better than the titanium-treated iron, the maximum permeability of the former being more than 20,000 compared to 9,000 for the latter. Again the hysteresis loss for $B = 10{,}000$ of electrolytic iron is about 800 ergs per cub. cm. per cycle compared to about 1,000 for the titanium-treated iron.[4]

On the other hand, Ti seems to increase the permeability of iron at high flux density, probably due to its reducing action on iron oxide. Thus for $H = 100$ the flux density of electrolytic iron is about 18,000, whereas that of the titanium-treated iron is about 19,000. However, silicon or aluminum accomplishes similar results without the danger of destroying the good magnetic properties should a trace of the deoxidizer be left in the alloy. At the Westinghouse Research Laboratory we have made a number of Fe-Ti alloys and check the results of the authors in regard to the effect of Ti when enough is added to leave metallic Ti in the iron. The result is a decided lowering of the permeability and

[1] Research Laboratory, Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.
[2] Engineering Exp. Stu., Univ. of Ill. Bull. No. 72, 1914.
[3] Eng. Exp. Stu., Univ. of Ill. Bull. No. 83, 1915, pp. 35 and 40.
[4] ergs per cub. cm. per cycle $= 173 \times 10^3$ joules per pound per cycle.

increase in the hysteresis loss. The only advantage of Ti seems to be the increase obtained in the electrical resistance; in this respect it has even a greater effect than Si or Al.

M. A. HUNTER (*Communicated*): I am inclined to think that the comparison made by Dr. Yensen between the results obtained by the treatment of iron with silicon and titanium respectively is not quite a fair one. In the first case it must be borne in mind that he started with iron which had been twice electrolytically refined, whereas our material was a commercial Norway iron. Again in Yensen's method of melting the material was maintained for two hours in a fairly good vacuum. With our material the melting operation was complete in 15 minutes starting from the cold charge. The first is a smelting and refining operation, the second purely a melting one. I have no information on the effect of titanium on the superfine grades of iron melted under the exacting conditions of Yensen's experiments. Our results do, however, show that a commercial iron is materially improved when small additions of titanium are made during the melting operation.

Incidentally, the maximum permeability obtained in our second series of melts was about 15,000 and not 9,000 as stated in Dr. Yensen's remarks.

The relative merits of the addition of titanium and silicon or aluminum would seem to be still an open question. Titanium is undoubtedly a more active scavenger than either of the other metals mentioned. We are convinced, however, that its addition must be carefully controlled.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

BRONZE PLATING.[1]

By F. C. Mathers[2] and Stanley Sowder.[3]

Abstract.

Bronze, a copper-tin alloy, can be plated or electro-deposited from the oxalates of copper and tin dissolved in ammonium oxalate or from a mixture of potassium copper cyanide, potassium stannate, potassium cyanide, and potassium hydroxide. The bath containing cyanide is better. A careful adjustment of the relative quantities of copper and tin in the baths is necessary. Most trouble is caused by the poor corrosion of the bronze anodes.

Review of the Subject.

Bennett[4] has given the formulas of the bronze baths that have been described in the literature. He states that practically all of them are impracticable. Commercially the bronze color is imitated with brass or by coloring with a reagent.

Treadwell and Beckh[5] have tried out several different baths. They obtained bronze deposits from the oxalates of copper and tin dissolved in potassium oxalate, and from a mixture of potassium copper cyanide and sodium sulpho-stannate (Na_2SnS_4).

They were unsuccessful with the potassium-copper cyanide and sodium stannate bath,[6] obtaining principally a copper deposit. In most of their work, electrolysis of a bath was only continued for a short time, and platinum anodes were used. In commercial work the bath must operate for long periods of time with only easily

[1] Manuscript received January 14, 1920.
[2] Assoc. Professor of Chemistry, Indiana University.
[3] Indiana University.
[4] Trans. Amer. Electrochem. Soc. (1913), 23, 255.
[5] Zeit. Elektrochem. (1915), 21, 374.
[6] Kremman D. R. P. 167718. Monatsh., 35; thru Chem. Abstr. (1914), 8, 2118.

made adjustments. Moreover, bronze anodes should be used and they must dissolve with near to theoretical efficiency, otherwise the composition of the bath cannot be maintained.

Kremann, Suchy, Lorber and Maas[6] also obtained satisfactory deposits from a bath of sodium tartrate, stannic chloride, copper sulphate, and sodium hydroxide. However, this bath soon became useless due to the decomposition of tartrate at the insoluble or passive copper anodes.

Manipulation.

Two anodes (90 percent copper and 10 percent tin), 4 by 4 cm. (1.6 by 1.6 in.) were used in each bath of 200 c.c. (½ pint). The single cathode in each bath was 4 by 4 cm. The temperature was 40° to 50° C. At low temperatures the anode corrosion was less good. The current density was 0.4 amp. per sq. dm. (3.75 amp. per sq. ft.). A decrease in current density increased the proportion of the more easily deposited constituent: copper in the oxalate bath and tin in the cyanide stannate bath.

Experiments.

Oxalate Baths. The bath recommended by Curry,[7] 5.5 percent ammonium oxalate, 1.5 copper sulphate, 0.42 stannous oxalate and 0.5 oxalic acid, gave a bronze deposit for a short time, but continued electrolysis gave only hard brittle copper, due to the poor corrosion of the anodes. The 5.5 percent ammonium oxalate will dissolve much more copper and tin than the quantities used, hence experiments were made with more concentrated baths. The copper sulphate was made as high as 3.5 percent, the stannous oxalate 2.5 percent, the oxalic acid was varied from 0 to 2 percent, and the ammonium oxalate was made as high as 6.5 percent. Satisfactory baths were not obtained in any case. Sufficient tin did not dissolve from the bronze anodes, but a slime rich in tin formed upon the anodes. This was an unexpected source of trouble since tin anodes had been found to dissolve with practically theoretical efficiency in an ammonium stannous oxalate bath.[8]

Various additions, such as tartaric acid, boric acid, citric acid, sulphites, potassium chloride, magnesium sulphate, ammonium

[6] Kremman D. R. P. 167718. Monatsh., 35; thru Chem. Abstr. (1914), 8, 2118.
[7] Jour. Phys. Chem. (1906), 10, 515.
[8] Mathers and Cockrum, Trans. Amer. Electrochem. Soc. (1916), 29, 411.

chloride, ammonium citrate, hydrogen peroxide, alcohol, peptone, glue, gum arabic, and potassium sulphate, produced no improvement with bronze anodes. Ammonium citrate and potassium sulphate used with the ammonium oxalate gave good corrosion efficiencies with pure copper anodes but not with bronze anodes. The only method found of maintaining the composition of the bath was as follows: A 500 c.c. bath containing ammonium oxalate 6 percent, copper oxalate 2 percent, ammonium citrate 1.6 percent, potassium sulphate 1.2 percent, and citric acid 0.4 percent, was electrolyzed with copper anodes. A 50 c.c. portion of the bath was removed and treated with strips of pure tin, whereby copper was precipitated and tin went into solution. Every few hours, a fresh 50 c.c. portion of the bath was removed for treatment with the tin and the previous portion was filtered and returned to the bath. In this way the ratio of copper and tin in the bath was kept sufficiently constant to give nice bronze cathode deposits. One of these small baths was kept in almost continuous operation for two months and good bronzes were obtained during the entire time.

Cyanide Baths. Very good deposits were obtained from a bath containing potassium hydroxide 5 percent, potassium cyanide 0.5 percent, stannic ammonium chloride 0.38 percent, and potassium copper cyanide 1.5 percent. The bronze anodes remained clean and bright and were never coated with slime. For several days only copper was deposited from a new bath. The reason for this non-deposition of tin during this period may have been that reduction to the stannous state was necessary. This preliminary induction period is perhaps the reason that some experimenters have reported failures with baths of this general composition. Any increase in free cyanide decreased the rate of copper deposition, hence gave a tin-colored deposit. The use of too much free cyanide is one of the difficulties with many of the baths described in the literature. No difficulty was encountered in the operation of this bath.

In another bath,[5] using a mixture of stannic sulphide dissolved in sodium sulphide and potassium copper cyanide, the anodes did not corrode well and principally copper was deposited. Treadwell and Beckh had found that bronze anodes did not corrode properly in baths of a similar composition but they were able to obtain

a bronze deposit upon the cathode. Their experiments were run only for short intervals of time.

All of these experiments were carried out several years ago, hence the use of potassium compounds. Without question the corresponding sodium compounds would work just as well.

SUMMARY.

Bronze can be deposited from a bath containing potassium hydroxide 5 percent, potassium cyanide 0.5 percent, ammonium stannic chloride 0.38 percent and potassium copper cyanide 1.5 percent. Satisfactory corrosion of bronze anodes is obtained, using a temperature of 40° to 50° C., and current density of 0.4 amp. per sq. dm. (3.75 amp. per sq. ft.).

Bronze can also be deposited from a bath containing copper oxalate and tin oxalate dissolved in ammonium oxalate, together with some potassium sulphate, citric acid, and ammonium citrate or similar salts. Bronze anodes will not corrode properly, hence copper anodes must be used. The tin content of the bath can be maintained by regularly precipitating the copper from a portion of it by using metallic tin.

Indiana University,
Bloomington.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

INFLUENCE OF ENCLOSED SLAG ON THE CORROSION OF WROUGHT IRON.*

By L. T. Richardson.†

There exists at the present time a controversy relative to the factors that enter into and influence the corrosion of wrought iron. A study of the technical articles relating to the subject, on the one hand, and advertising literature on the other, shows that this controversy obtains only to a rather limited extent among purely scientific investigators of the corrosion of metals, but exists almost entirely among the manufacturers of different brands of iron. In view of this controversy, it was considered to be of more than passing interest to conduct experiments that might throw some light upon certain of the factors that are contended to greatly influence the corrosion of wrought iron. The conclusions arrived at in this article are based upon these experiments.

The factors that enter into or at least are claimed to enter into the corrosion of wrought iron and which, moreover, are asserted to be the cause of its superiority as a rust-resisting material over other forms of iron are closely connected with the corrosion of ancient iron objects that have been exposed to the elements for years or centuries, for investigations have shown these objects to be wrought or puddled iron.

For instance, Sir Robert Hadfield[1] examined several specimens of ancient iron, particularly the iron pillar at Delhi, India, and several iron implements of Sinhalese origin and concluded from an analysis and a microscopic examination that they were some form of wrought iron.

Walter Rosenhain[2], another investigator, tested a piece of ancient iron from Ceylon and found that it was similar in structure to wrought iron.

* Manuscript received January 22, 1920.

† Chemical Engineer, New Brunswick, N. J.

[1] See references at end of paper.

Likewise Dr. Hjdmar Braune[3] described a prehistoric iron object found at Castanela, Switzerland. From a chemical and a microscopic analysis he concluded that it was an almost pure iron that had never been in the molten state. Similarly other investigators[4, 5, 6, 7] have recorded investigations of old irons 50 to 150 years of age that have proven to be wrought iron.

It seems almost certain, then, from these published accounts that those ancient iron objects which have shown such a remarkable resistance to corrosion are made of puddled iron, and it is therefore only natural to expect that iron manufacturers of today in their search for a corrosion resisting material should attribute the rust-resisting qualities of these old irons to just those properties that characterize wrought iron itself. These distinguishing properties are two in number, a chemical one that the iron is quite pure, and a physical one that the iron has long layers or threads of slag or cinder scattered throughout its mass. Wrought iron we may then describe as consisting largely of pure iron throughout whose mass are scattered long threads or sheets of slag or cinder. Some even go so far as to say that each fiber is coated with an almost infinitesimal film of slag[9, 10]. It almost follows that because of these two different characteristics, the resistance of wrought iron to corrosion should be ascribed to two different causes by two classes of observers—one claiming that the resistance of wrought iron to corrosion is due mainly to its chemical purity; the other contending that it is due to its physical structure.

The exponents of the chemical theory contend that the resistance of wrought iron to corrosion, as well as the specimens of ancient iron, is due to the purity of the iron and hence that any iron that would duplicate the purity of the metal in the old irons would likewise be resistant to corrosion. The virtues of "ye olde time" irons they say are due to their purity and advocate pure iron as a "return to ancient virtues." [4, 8].

The believers in the physical theory, on the other hand, contend that the resistance of wrought iron to corrosion is due mainly to its physical structure and in particular to the form and distribution of its slag contents. They say that the method of manufacture is the important factor, for due to the fact that the iron never becomes molten in the puddling furnace quantities of slag are incorporated with the metal. The structure is similar to a

FIG. 1.

FIG. 2.

FIG. 3.

bundle of compressed twigs in which each fiber of iron is covered and protected by a bark-like layer of slag. They claim that the slag is more rust-resistant to corrosion than is pure iron and forms a barrier as rusting penetrates into the metal, so that on reaching each slag inclusion the oxidation must take another course and begin anew.[9, 10, 11, 12] The adherents of this theory, therefore, advocate the use of wrought iron as the means of "defeating rust."

The remarkable part of the whole controversy is that neither side gives any direct and definite proof that their contention is true. For instance, the adherents of the pure iron theory do not show that pure iron metal with slag rusts equal to or faster than pure iron itself, nor do the adherents of the physical structure theory show that the metallic iron in wrought iron rusts faster without the slag than with it. This is probably due to the fact that it is impossible to separate the iron from the slag without destroying its identity. Thus it would be impossible to remove the slag from wrought iron without a melting process which would change its nature since puddled iron has never been in a molten state, and it would be just as impossible to introduce slag into pure iron without some such similar treatment.

The very structure of wrought iron, however, offers a means of testing, to a certain extent, these two theories without disturbing the relation of slag and iron or changing the nature of either. This structure is shown clearly in Fig. 1 and Fig. 2—a longitudinal and a transverse section respectively in which the slag inclusions appear as dark lines in the former and as dots in the latter. It is easily seen that in one direction, namely, perpendicular to the slag layers, the metal is not continuous and any oxidation of the metal as it penetrates inwardly from the surface must meet layers of slag. In the other direction, however, that is, in a direction parallel to the layers of slag, the metal is continuous and as it penetrates will not meet these layers of slag or cinder. Hence, if corrosion is retarded by slag inclusions, as is insisted upon by the adherents of the physical structure theory, one would expect to find that transverse sections of wrought iron will rust more rapidly than longitudinal sections. On the other hand, if the two sections corrode at the same rate we may conclude that as far as producing any physical obstruction to corrosion is concerned, the slag is inert and that any property of resist-

ing corrosion that wrought iron may possess is not due to slag barriers but the purity of the metal or to some other cause.

In order to test out this line of reasoning, transverse and longitudinal sections about 1/16 inch in thickness were taken from pieces of Swedish iron and wrought iron and subjected to rusting at different times. The pieces were thoroughly annealed and the surfaces made smooth with emery cloth. After weighing and measuring the thickness of each piece in several places, all were placed in a wooden rack, as shown in Fig. 3, and exposed to the weather as follows:

Wrought iron (A and B).....1 year
Swedish iron .....6 months
Wrought iron (C).....2 years

The analysis of the different irons, the exposure data and the results are given in Table I and Table II.

TABLE I.

	Sulphur	Phosphorus	Carbon	Manganese	Silicon	Copper
Steel	0.032	0.079	0.08	0.56	....	none
Wrought Iron (A)	0.044	0.132	0.015	0.095	0.193	none
Wrought Iron (B)	0.020	0.100	0.020	0.038	0.180	none
Swedish Iron	0.015	0.052	0.015	0.011	0.050	none
Wrought Iron (C)	0.026	0.115	0.04	0.05	0.210	0.10

TABLE II.

	Time Exposed	Transverse Section		Longitudinal Section	
		Loss in Weight	Depth Pits	Loss in Weight	Depth Pits
Steel					
Wrought Iron (A)...	6 mos.	0.1178	0.035	0.1101	0.033
Wrought Iron (B)...	6 mos.	0.0791	0.044	0.0789	0.041
Swedish Iron	6 mos.	0.1068	0.026	0.1333	0.026
Wrought Iron (C)...	2 years	0.153	0.020	0.154	0.025

In the above table the loss in weight is in grams per square centimeter and was obtained by cleaning the rusted specimens with a solution of ammonium citrate. The depth of pits was obtained by grinding the surface of the cleaned specimens until the pits on the surface were removed.

It is evident from these figures that the amount of total corrosion as given by the loss in weight, as well as the extent of localized corrosion as indicated by the depth of pits, is the same in both transverse and longitudinal sections within the limits encountered in corrosion work.

In order to determine definitely, however, that the slag inclusions offered little resistance to corrosion, it was necessary to show that corrosion actually penetrated layers of slag. To settle this point sections were made of the iron test pieces and examined with a microscope. A representative section is shown by Figs. 1 and 2 which are photographs that include an area 1.5 millimeters in diameter. Since in some cases corrosion had penetrated 0.35 to 0.44 millimeter, it is evident that several layers of slag had been penetrated.

In addition to these data, sections of the specimens have been carefully examined with a microscope and in no case has any visible evidence been found of slag inclusions hindering the progress of corrosion. Likewise, an examination of the corroded surfaces of a number of old irons that have been exposed to corrosion for ten to thirty years, failed to show any evidence of slag in wrought iron retarding the progress of corrosion.

In view of the fact that the corrosion of transverse and longitudinal sections is the same as regards loss in weight and depth of pits, the conclusion has been reached that any superior resistance to corrosion that wrought iron may have is not due to slag inclusions but to some other cause, among which may be mentioned the purity of the iron. Furthermore it is our experience that the "pure irons" on the market are very similar to wrought iron in their resistance to corrosion. This would also tend to confirm the above observation.

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DISCUSSION.

J. A. AUPPERLE[1]: I am interested in the subject under discussion, and wish to compliment the author on his study of the problem by making atmospheric exposure tests of both transverse and longitudinal sections of wrought iron.

Mr. Richardson's statement on page 531 is in error, where he states that "puddled iron has never been in a molten state." This method is sometimes called the pig-boiling process on account of the molten condition of the iron in the early stages of the operation. During the later stages when the impurities have been oxidized the iron "comes to nature," and becomes pasty on account of it having a higher melting point than the impure iron used in the process. After coming to nature the pasty mass is collected in balls, removed from the furnace and squeezed to remove most of the slag.

I am in accord with the author's statement that purity of iron is essential to long life.

The author has not given either the oxygen or slag content of the samples tested. If the slag had been shown by the microscope on all samples instead of only one it would have made the comparison of more value. The iron of the pillar of Delhi, India, already referred to, contained very little slag. The iron was determined by the direct method. The analyses of several specimens of ancient irons are given in Table I.

[1] Chief Chemist, American Rolling Mill Co., Middletown, Ohio.

All of the above irons were made by the charcoal process and contained very little slag, which seems to corroborate Mr. Richardson's claims that the presence of slag is not the reason for the long life of ancient irons, and that it is on account of their purity.

In our research work we have studied the gas content of iron and steel and the influence of gases upon the rate of corrosion. In the above examples the nitrogen content will be found extremely low. In fact, I have never analyzed an ancient iron without finding low nitrogen. This is undoubtedly due to the method of manufacture which precludes the possibility of a high nitrogen content. It is my opinion that the nitrogen content exerts a greater influence upon the rate of corrosion than any other element.

TABLE I.

	Si	S	P	C	Mn	Cu	O	N	Cu, O etc.	Fe
Iron pillar, Delhi. India..... (1600 years old)	0.046	0.006	0.114	0.080	Nil	....	....	....	0.034	99.72
Iron rails from Fairbank's House, Dedham, Mass..... (281 years old)	0.029	0.009	0.005	0.015	0.020	0.016	0.060	0.005	.....	99.841
Link from bridge at Newburyport, Mass..... (100 years old)	0.028	0.014	0.023	0.040	0.008	Trace	0.027	0.003	.....	99.867

In contrast with durable irons we have numerous examples of steel which failed in a very short time. All of those which failed in a short time were found to be high in nitrogen. We have had 26-gauge (0.48 mm.) Bessemer sheets, which were exposed to the weather, fail within 13 months; other sheets of the same gauge lasted 34 months. Typical analyses of the good and poor Bessemer sheets are shown in Table II.

It will be noted from this table that the nitrogen content of the poor sheet is more than three times as great as in the good sheet.

Most failures of steel under normal conditions can be attributed

to the high nitrogen content, although carbon monoxide gas also exerts a deleterious influence.

In Table III will be found the analysis of a pipe and a spike which in addition to containing high nitrogen also contain a high percentage of carbon monoxide. We have also included the analysis of pure iron made in an open-hearth furnace for the purpose of showing that the nitrogen content in the above failures

TABLE II.

	C	Mn	P	S	Cu	CO	O	N
Good Bessemer Sheet No. 624	0.010	0.480	0.082	0.044	Trace	0.021	0.055	0.006
Poor Bessemer Sheet No. 531	0.015	0.310	0.060	0.063	0.010	0.015	0.071	0.019

TABLE III.

	C	Mn	P	S	Si	Cu	N	O	CO
Pipe which failed in alkali soil after 14 months.....	0.090	0.357	0.098	0.049	Trace	0.014	0.041	0.032	0.052
Spike which failed in railroad tie (Arizona) after 9 years	0.100	0.405	0.108	0.041	Trace	Trace	0.033	0.082	0.058
Pure iron made in open hearth furnace	0.010	0.025	0.004	0.025	Trace	0.004	0.004	0.015	0.015

is ten times as high as the nitrogen content of pure iron. This comparison also shows that the carbon monoxide is several times higher in the pipe and spikes which failed than in the pure iron.

Based upon the data which we have accumulated, we find the gaseous impurities have a greater influence upon the rate of corrosion than the solid impurities.

As far as the influence of slag in wrought iron is concerned, we have been able to dissolve the slag from a sample of puddled iron as shown in Fig. 1. Both the puddled iron and the iron

made in an open-hearth furnace were submerged for half their length for two hours in 25 percent sulphuric acid. The pure iron bolt was attacked but slightly. The slag in the puddled iron bolt had modified the attack to such an extent as to indicate the fibrous nature of the product. This test seems to confirm what

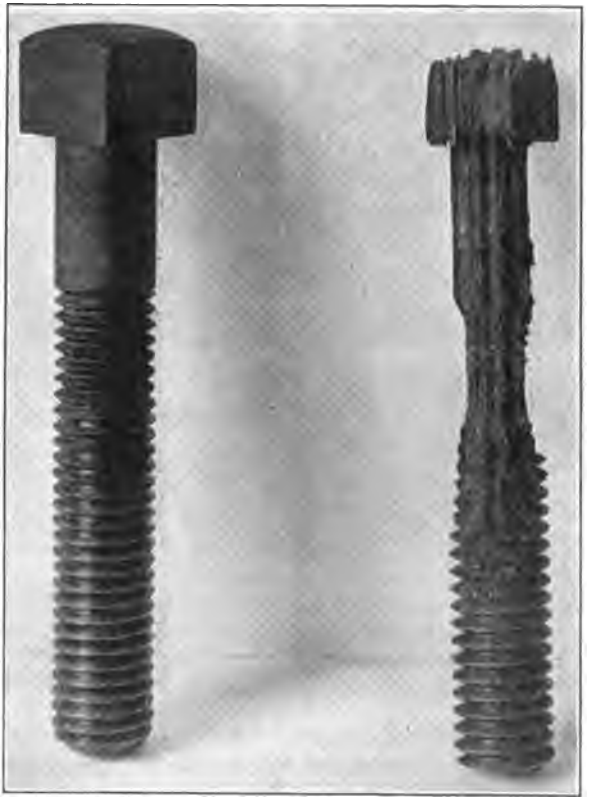

FIG. 1.

Open-hearth furnace pure iron bolt. Puddled iron bolt.

Mr. Richardson has said about the slag offering no protection from a corrosion resisting standpoint.

The puddled iron contained much more slag than the one shown in Mr. Richardson's paper, and for the purpose of comparison, I am showing also the longitudinal and cross-section of a sample

of pure iron made in an open-hearth furnace. The latter consists essentially of ferrite and is free from slag.

JAMES ASTON[2] (*Communicated*): The quite generally admitted merit of wrought iron in withstanding usual corrosion may be attributed to four fundamental characteristics, as follows:

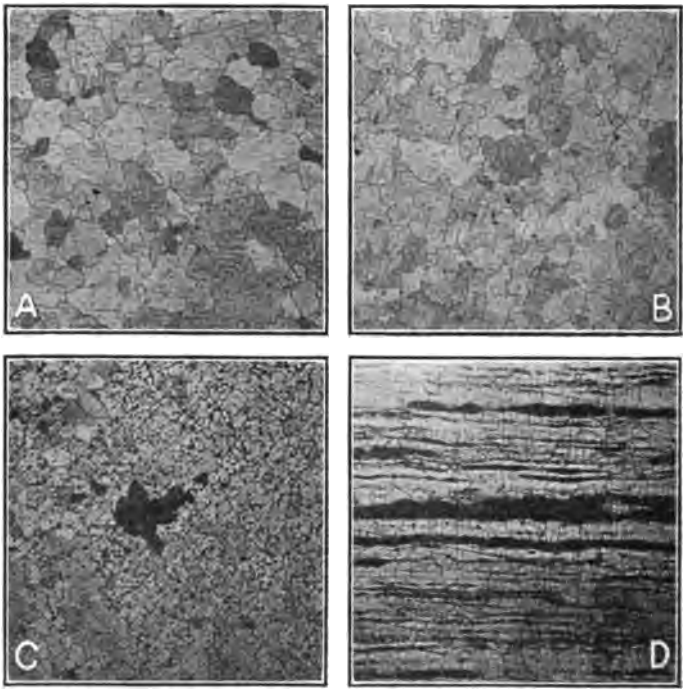

FIG. 2. PHOTOMICROGRAPHS OF BOLTS SHOWN IN FIG. 1.

A. Transverse Section of Open-Hearth Furnace Iron Bolt Ferrite.
B. Longitudinal Section of Open-Hearth Furnace Iron Bolt Ferrite.
C. Transverse Section of Puddled Iron Bolt Ferrite and Slag Inclusions.
D. Longitudinal Section of Puddled Iron Bolt Slag Lines.

1. The chemical purity of the base metal.

2. The barrier action of the slag inclusions in obstructing the progress of corrosion.

3. The mechanical influence of the slag net-work in holding the rust more tenaciously or in densifying its usual character.

[2] Metallurgist, A. M. Byers Co., Pittsburgh, Pa.

4. An indirect effect of the slag, of a chemical nature, in changing the characteristics of the rust, and thus disturbing or tending to neutralize the usual electrochemical relations of rust and iron.

It is exceedingly difficult, perhaps even impossible, to gather direct evidence regarding the relative importance of the above functions. I am of the opinion, based upon extended observation and upon experiment of an indirect nature, that while the chemical constitution of the base metal is an important contributing factor, the essential feature underlying the merit of wrought iron is the slag incorporation. Since Mr. Richardson considers only one of the three influences which the slag may exert, namely its barrier action, his conclusion "that any superior resistance to corrosion that wrought iron may have is not due to slag inclusions, but to some other cause," is obviously far-fetched, even granting that his reasoning is sound.

I believe that Mr. Richardson's argument is based upon a false hypothesis, and upon a distorted sense of proportion. His data, therefore, while they might be interpreted to confirm his assumption, contribute nothing in proving the facts. The base metal of wrought iron is not discontinuous in a direction perpendicular to the slag layers, and continuous in a direction parallel to them, as is the assumed basis of his argument. That rolling tends to elongate the slag to a semblance of threads or ribbons, is true; such general continuity, however, is of very small, even microscopic dimensions. To fully appreciate the true condition, we must realize that the slag distribution is from 250,000 to 1,000,000 filaments per square inch, or a finite distance of separation of 1/500 to 1/1000 inch. There is no such condition as a layer of slag separating layers of iron, or a continuity of metal or slag in a transverse section as contrasted with the reverse condition in a longitudinal direction. There may be a simulation of pointedness of slag in a transverse direction, and stringiness in the longitudinal; this is not an essential of wrought iron, but only an incident of the manner of working.

The Pillar of Delhi no doubt consists of a mass of blooms which have had fairly equal work in all directions, with accompanying uniformity of slag characteristics. As a piece of wrought iron, is it any the less effective on this account in weathering the

attack of the elements? Or do the flakes of graphite in cast iron lose their effectiveness because they have not had the benefit of a rolling or forging operation to elongate them in one particular direction?

With modern rolling processes, there will be elongation of the slag in one direction. How much the difference in corrosion resistance perpendicular to the slag filaments is thereby increased as compared with a parallel direction, is a doubtful point which is hardly to be cleared up by meager figures of loss of weight or depth of pits, in the uncertain stage or with the lack of standards prevailing in corrosion measurements today. Mr. Richardson's data lead to no definite conclusions on the point in question.

FRANK HODSON[3] (*Communicated*): Mr. Richardson's paper certainly demonstrates that the corrosion of iron is unaffected by the direction in which the samples are cut, *i. e.*, traverse or longitudinal sections, and from this it may be reasonably deduced that the infinitesimal film of slag—which may or may not surround the iron fibres—does not exercise a very important bearing on the rate of corrosion. The evidence would seem to point to the fact that the influence of carbon and other elements may be much more important.

Tests I made some years ago on steel, results of which were given before the British Association, proved a definite corrosion curve governed by the contents of carbon. Tests were made on standard sized pieces, under all conditions of corrosion, weather, sea and fresh water, and acids. Tests were then made on steels with varying percentages of carbon and increasing percentages of chromium, nickel, manganese, silicon, etc. In these alloy steels the influence of the carbon content was found to be replaced by the new alloy.

I believe a very large field for investigation lies before the research student, who will work on similar lines with iron—taking as a base pure "American Ingot Iron" and adding varying percentages of chromium, nickel, manganese, etc. This would conclusively prove that the influence of the elementary constituents, and not the method of manufacture, controls the rate of corrosion.

Mr. Richardson may have particulars of the analyses of some of the ancient irons; if so, I should be interested to know whether

[3] Pres., Electric Furnace Construction Co., Philadelphia, Pa.

any of them which have proved so resistive to corrosion contained appreciable amounts of nickel, copper, manganese, or chromium.

L. T. RICHARDSON (*Communicated*): The statement, "puddled iron has never been in the molten state," I believe to be correct. The pig iron from which the puddled iron is made is in the molten state in the early stages of refining, but the puddled iron itself does not come into existence until the melt "comes to nature."

Mr. Aupperle has somewhat misinterpreted one of the statements when he says that the article states that purity is essential to long life. All that we have said is that any superiority that wrought iron may have as a rust resisting metal may perhaps be due, among other causes, to its purity. In fact, recent tests would indicate that extreme purity is detrimental to long life.

We do not believe that gas content has any great influence on the corrosion of iron, as Mr. Aupperle would indicate. To our knowledge no data exist to warrant drawing any such conclusions. If such data exist, in the interest of science they should be published.

Mr. Aston believes that the paper is based upon a false hypothesis. He states that at least four factors enter into the corrosion of wrought iron. Factor (1) relates to the purity of the iron; factor (2) to the barrier effect of the slag, and factors (3) and (4) to the effect of the slag inclusions in changing the character of the rust. Tests made by the American Society of Testing Materials show that wrought iron free from copper does not have an adherent rust film, that is, the presence of slag does not change the character of the rust. This disposes of factors (3) and (4) and leaves (1) and (2) which are just those that we are discussing.

Some of the ancient irons show traces of copper and nickel, but only traces. They are free from manganese. As to the effect of various elements upon the corrosion of pure iron we would refer Mr. Hodson to the work of Burgess and Aston given in Journal of Industrial and Engineering Chemistry, June, 1913.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

THE EMBRITTLING EFFECTS OF CLEANING AND PICKLING UPON CARBON STEELS.[1]

By S. C. LANGDON[2] AND M. A. GROSSMAN.[3]

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[1] Published by permission of the Director of the Bureau of Standards. Manuscript received February 16, 1920.

[2] and [3] Formerly with the Bureau of Standards, Washington.

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I. INTRODUCTION.

It has long been recognized that in the pickling and plating of steel there is a tendency to produce changes in the mechanical properties of the steel and especially to cause brittleness. Except for articles such as springs, however, upon which the embrittling effects may be very pronounced, comparatively little attention has been paid to this subject in commercial practice. This condition is probably due to the fact that most of the steel articles in common use have such a large factor of safety that any such effects would be negligible, or at least appear to be so, and also that these effects are largely temporary. In connection with the manufacture of military supplies, and especially of airplane fittings for which it was desired to have the maximum strength for the minimum weight, this question assumed considerable importance. Unfortunately very few data were available from which even the magnitude of the various effects could be determined. With the many problems then on hand at the Bureau of Standards, it was possible to conduct only a few experiments, from which very general conclusions and recommendations were made. In consequence of the lack of exact knowledge upon the effect of pickling and plating operations, there was no doubt considerable hesitancy in adopting protective coatings such as zinc plating, which were admittedly superior to many of the coatings actually used.

As soon as conditions permitted, a more extensive investigation of this subject was undertaken, the results of which are presented in this paper. As the work progressed it became evident that the problem is very complex, and will require the study of many additional factors before exhaustive data can be obtained or conclusive explanations or remedies can be suggested. Many of the results contained in this paper are therefore only of a preliminary or qualitative nature. As originally planned it was expected to include in the investigation the effects both of pickling and plating.

Unfortunately, however, the work was necessarily interrupted at a time when the data upon plating were very incomplete. This paper is therefore confined to a description and discussion of the effects of cleaning and pickling processes, such as are used preparatory to plating or other coating operations.

While the methods employed in this investigation for the removal of grease and scale were so far as possible similar to those used in commercial practice, no attempt was made to study their efficiency as cleaning methods. The conditions employed should therefore be understood to be typical rather than recommended methods.

II. REVIEW OF PREVIOUS WORK ON PICKLING.

Attention has for years been called to the embrittling of steel by acid, as encountered for example in the cleaning of surfaces preparatory to the application of protective coatings. While there is no account in the literature of any series of experiments to show definitely the relative effects of the various pickling methods, there have appeared certain series of experiments which are very illuminating. One of the best was published as early as 1875,[4] the tests being carried out mostly on wrought iron wire and some on steel wire. Iron wire was made brittle by immersion in acid, as shown by a decrease in the number of bends it would withstand before breaking. If immersed in water while still hot from bending, minute bubbles could be seen (with a microscope) to arise from the fracture. When the wires were left at 16° C. (61° F.) for three days, or heated at 200° C. (392° F.) for half a day, they regained their toughness. Johnson also found a loss in weight when pickled iron was annealed.

All this pointed to the theory of the occlusion of hydrogen in iron. Hydrogen was also found occluded when iron was made the cathode in an electrolytic cell, and the same effects of brittleness and bubbling could then be detected. Tension tests (these were employed because "in the case of the diminution of toughness, no exact and easily applied test has yet been devised") were made on both annealed and bright iron wire after "one hour in hydrochloric acid" and "twelve hours in very dilute hydrochloric acid," and compared with tests on wires similarly treated but then

[4] Johnson, Proc. Royal Soc. (1875), 23, 168.

heated 12 to 48 hours to expel hydrogen. The former had lower tensile strength and less elongation. Johnson also found that the presence of hydrogen in wire increased its electrical resistance. Diffusion of hydrogen in iron was shown by immersion of a wire in acid with half its length protected, diffusion taking place in iron to six times the extent it did in steel.

Cailletet[5] showed the extreme brittleness of electrolytic iron to be due to occlusion of hydrogen.

Ledebur[6] quotes Hughes,[7] who reported that brittleness was produced in iron after 30 minutes in dilute sulphuric acid, or after two minutes in the same acid if connected with zinc. The zinc protects the iron from attack by acid, but promotes evolution of hydrogen at the surface of the iron, which proves that the brittleness is due not to attack by acid but to hydrogen. Ledebur reports that brittleness is induced by immersion in 2.5 percent acid for 23 hours, 0.5 percent acid for 98 hours, or in contact with zinc in 2.5 percent acid for three hours. When tested immediately, there was considerable reduction in the "bending quality" and in elongation in tension test; but when held four days before testing, the values were found to be partially restored. Heating to cherry red restored nearly the original values. The embrittling effect produced by a vigorous electrolytic pickling was removed when the iron was allowed to lie for four weeks in a dry place. Brittleness was induced by 24 or 72 hours immersion in mine water containing acid or by two months rusting in the air, causing a reduction in the transverse strength of 1-in. (2.5 cm.) square bars. Ledebur also determined the hydrogen content of pickled steels.

In 1889 Ledebur gave evidence confirming his previous work[8] and made further pickling experiments in which all pickling was done in contact with zinc in 3 percent sulphuric acid. Silicon in the steel seemed to reduce the liability to pickling brittleness, while carbon seemed to promote it.

Roberts-Austen[9] demonstrated that iron which has been made the cathode during electrolysis will exhibit the hydrogen points in a heating curve determination.

[5] Compt. rend. (1875), 80, 319.
[6] Stahl und Eisen (1887), 7, 681.
[7] Brit. Assn. Telegraph Engrs. (1880).
[8] Stahl und Eisen (1889), 9, 745.
[9] Proc. Inst. Mach. Engrs. (1899), 36.

Heyn[10] discusses brittleness and the dry absorption of hydrogen by iron at high temperatures. Brittleness of the iron disappears on standing some weeks in the cold.

Burgess and Engle[11] show that unheated electrolytic iron is in an unusual state, from the fact that it dissolves in acid more rapidly even than does zinc. After heating to 1000° C. (1832° F.) the rate of solution is brought extremely low.

Longmuir[12] reports a very marked reduction in the toughness of rail steel, as tested in alternating stress, when cleaned and pickled by various methods. Inexactness in reporting conditions of treatment impairs the value of the evidence, but he covers a wide range of treatments in various acids, re-heating, sand-blasting and salt bath treatment.

Andrew[13] studied the embrittling effect of caustic soda on iron. He considers it due to the action of hydrogen in effecting a molecular re-arrangement.

Merica[14] and Parr[15] in considering boiler failures made further studies on the effect of sodium hydroxide solutions at various temperatures on steel. There was a considerable reduction of toughness in the alternating stress test, the change being attributable to hydrogen.

Coulson[16] compared anode and cathode pickling with ordinary pickling and found that cathode pickling had as serious embrittling effect as ordinary immersion, but that anode pickling caused no brittleness as measured by oscillation tests on springs and by tension tests.

T. S. Fuller[17] investigated the brittleness produced in steel springs by pickling and plating and recommended the preliminary coating of the steel with tin by hot dipping, before copper plating.

M. DeKay Thompson and O. L. Mahlman[18] made an investigation of the relative efficiency of electrolytic and ordinary pickling of steel, but did not make any experiments upon the brittleness caused by the pickling.

[10] Stahl und Eisen (1900), 20, 837.
[11] Carn. Inst. of Washington (1906), 5, 225.
[12] Jour. Iron and Steel Inst. (1911), (1), 163.
[13] Trans. Faraday Soc (1913), 9, 316.
[14] P. D. Merica, Met. Chem. Eng. (1917), 16, 496-503.
[15] S. W. Parr, Univ. of Ill., Eng. Expt. Sta. Bull. (1917), 94, 1-57.
[16] Trans. Amer. Electrochem. Soc. (1917), 32, 237.
[17] Trans. Amer. Electrochem. Soc. (1917), 32, 247.
[18] Trans. Amer. Electrochem. Soc. (1917), 31, 181

Watts and Fleckenstein[19] examined the effect of cyanide solutions in electroplating, and concluded that the embrittling effect was due to hydrogen, as no brittleness was found when no hydrogen was seen at the cathode.

Treischel[20] found that when steel was pickled in a 3 percent solution either of hydrochloric or sulphuric acid, the amount of hydrogen occluded in the steel was not sufficient to produce "blistering" when the steel was subsequently enameled. When however pickling was conducted in a 10 percent solution of either of these acids, blistering subsequently occurred.

In a recent investigation, T. S. Fuller[21] showed that hydrogen readily penetrates iron at temperatures from 20° C. (68° F.) to 100° C. (212° F.) whether the iron is pickled directly in 1 percent sulphuric acid, or is made the cathode in such acid. He explained his results by assuming that the initial penetration is due to the presence of atomic hydrogen, which subsequently combines within the iron, to form molecular hydrogen. The latter accumulates till the pressure is sufficient to force the hydrogen through the iron. The pressure thus produced is suggested as the cause of brittleness in pickled iron. Whether in the light of subsequent research this hypothesis is confirmed or not, the observations are of far reaching importance and throw light upon previously unexplained phenomena, such as the great effect of pickling upon steel of relatively large cross section.

III. MATERIALS EMPLOYED.

The steel used for the tests was in two forms, *viz.*, rods of various sizes and carbon contents, and strip steel of various grades and thicknesses. In view of the fact that all of these materials were of commercial sizes, expressed in ordinary English units, other measurements were made in the same units, with the exception of those with the Erichsen machine, which was calibrated in the metric system. For the sake of completeness all measurements will be expressed in both units, the first in each case being that in which the measurement was made.

[19] Trans. Amer. Electrochem. Soc. (1918), 33, 169.
[20] J. Amer. Ceramic Soc. (1919), 2, 774-81.
[21] Trans. Amer. Electrochem. Soc (1919), 36, 113.

A—Steel Rods.

TABLE I.

Size and Composition of Steel Rods.[22]

Stock No.	1	2	3	4	5	6	7
Diam. of Rod.. { inch	3/8	3/16	1/8	1/16	3/16	3/16	3/16
mm.	9.5	4.8	3.2	1.6	4.8	4.8	4.8
Carbon, percent	0.30	0.33	0.31	0.35	0.08	0.54	0.89
Manganese, percent.....	0.40	0.40	0.43	0.39	0.30	0.40	0.41
Phosphorus, percent....	...	0.032	0.034	0.031	0.012	0.033	0.029
Sulphur, percent.....	...	0.032	0.037	0.041	0.051	0.038	0.026
Silicon, percent.....	...	0.145	0.145	0.141	0.032	0.167	0.201

Table I shows the composition and diameter of the various steel rods. The stock numbers at the top of the columns will be used in referring to the different grades and sizes of rod. The stocks referred to as 1, 2, 3, and 4 are all from the same heat of steel and all were cold drawn to the sizes in question, annealed, and then straightened and cut. Thus there were available different sizes of stock of approximately the same carbon content.

The range from low to high carbon content for the same size rod is shown in stocks 5, 2, 6, and 7. The mill treatment for stock 2 has just been given. Stock 5 is of basic and stocks 6 and 7 of acid open-hearth manufacture. These rods (stock 5, 6, and 7) were annealed in coil at $\frac{3}{16}$ in. (4.8 mm.) diameter, straightened and cut. All samples of each given carbon content are from the same bundle of wire. This stock of rods was especially prepared for this research, and was remarkably uniform both in mechanical properties and in dimensions.

This marked uniformity of the stock as received made it quite satisfactory to run most of the tests on this stock without any subsequent heat treatment. Throughout this paper the comparison tests made on the stock as received from the manufacturer are designated as being made on "raw stock."

For purposes of comparison some of the stock was either hardened and tempered, or normalized. The heat treatments given in these instances will be detailed in connection with the tests made upon such materials.

[22] For the analyses of these and other steel specimens used in this investigation the authors are indebted to Mr. F. H. Tucker, of this Bureau.

B—Strip Steel.

TABLE II.

Size and Composition of Strip Steel.

Identification Letter	Reduction in Thickness After Annealing		Final Thickness		"Temper"	Carbon Per-cent	Manganese Per-cent	Phosphorus Per-cent	Silicon Per-cent	Sulphur Per-cent
	In.	Mm.	In.	Mm.						
A	.....	...	0.0126	0.32	Dead Soft	0.14	0.37	0.009	0.008	0.060
B	0.0010	0.03	0.0126	0.32	Quarter Hard	0.09	0.37	0.009	0.006	0.063
C	0.0040	0.10	0.0126	0.32	Half Hard	0.11	0.38	0.009	0.005	0.064
D	0.0074	0.19	0.0126	0.32	Hard	0.08	0.38	0.009	0.008	0.063
E	.....	...	0.0253	0.64	Dead Soft	0.09	0.37	0.007	0.006	0.060
F	0.0020	0.05	0.0253	0.64	Quarter Hard	0.08	0.37	0.007	0.004	0.060
G	0.0577	1.47	0.0253	0.64	Hard	0.08	0.37	0.007	0.004	0.062
H	.....	...	0.0358	0.91	Dead Soft	0.09	0.37	0.006	0.004	0.061
I	0.0030	0.08	0.0358	0.91	Quarter Hard	0.08	0.37	0.007	0.004	0.062
J	0.0472	1.20	0.0358	0.91	Hard	0.07	0.37	0.007	0.005	0.066

As shown in Table II the strip steel used was of low carbon content, of three different thicknesses and of several different grades of hardness, depending on the amount of cold work received, *i. e.*, the reduction in thickness produced by cold rolling after annealing. The various types of stock will be referred to by the identification letters given in the first column. Stock F was found to be very well adapted to this study, and was used in most of the experiments with strips. All of the stock was 3⅜ in. (8.5 cm.) wide and came from the manufacturer in long rolled strips. All except the dead soft had a smooth bright surface suitable for electroplating.

IV. METHODS OF TESTING.

A—Testing Rods.

At the outset of the investigation the direct determination of the elongation in the tension test was tried, but the changes produced were of too small a magnitude to be satisfactory for

measuring the brittleness produced by pickling steel. The impact test on notched bars could be rapidly made but had the disadvantage of requiring that the specimens be accurately notched. Extended tests with a modified Izod impact pendulum, designed especially to test the small rods, showed that the brittleness produced by pickling could not be measured by this method, since the effects, if any, were too small.

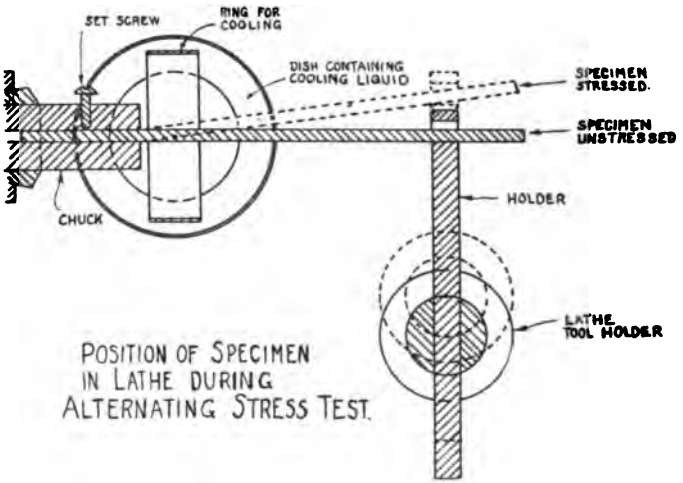

FIG. 1.

The test for rods which was finally adopted and which proved quite satisfactory was an alternating stress test. This test, which gave very marked effects due to pickling, was quickly and easily carried out with fairly uniform results, and could be made on short sections of any size rod without any preparatory machining. No extensive special apparatus was required. The set-up (Fig. 1) consisted of an ordinary bench lathe to which could be fitted simply constructed chucks, one for each size of rod tested; and a holder which was clasped in the tool seat and which was used to push the free end of the rod a definite distance off centre, thus causing the rod to be stressed in all directions when the lathe was in motion. The holder consisted simply of a piece of steel with a hole drilled through it slightly larger than the diameter of the rod. At the beginning of an experiment the hole in the holder was

centered up accurately with the revolving chuck, then set so that its nearest edge was 2.75 in. (7 cm.) from the chuck. Then by means of a graduated screw the holder could be set for any degree of eccentricity.

Throughout the tests the rods were kept as cool as possible by having the stressed region constantly moistened with alcohol. This was accomplished by hanging over the rod a large wide ring the lower part of which dipped into alcohol. (See Fig. 1). When the test bar was in rotation this ring was kept continually moving and thus carried a fresh supply of alcohol to the rod. Without some such device the rods became quite hot on being tested and yielded results which were not so uniform. So far as could be observed the alcohol had no effect upon the brittleness produced by pickling.

The distance between the chuck and the holder was 2.75 in. (6.99 cm.). The degree of eccentricity for the $\frac{3}{16}$ in. (4.8 mm.) rods was 0.25 in. (6.4 mm.) and for the $\frac{1}{8}$ in. (3.2 mm.) rods was 0.40 in. (1 cm.). These rods were 4.5 in. (11.4 cm.) in length. All except the large $\frac{3}{8}$ in. (9.5 mm.) rods were tested on the bench lathe. These latter rods, which were 8 in. (20.3 cm.) long, were tested on a larger shop lathe, in which they were held in an ordinary three jaw chuck. The distance between the chuck and holder was 6 in. (15.2 cm.) and for the test the holder was forced 0.5 in. (1.3 cm.) off center.

In all cases the period of stress was counted from the time the switch was closed, thus starting the motor, to the time of break of the specimen. For the small rods (raw stock) this required about one minute, while the large rods (raw stock) required two to four minutes. The time required to break a given type of specimen was not always the same, due to differences of speed of the motor and the slight wearing of the holder. These were found to be negligible for a given day's run, but for tests carried out over a long period of time the absolute values would not be comparable. Errors from this source were avoided by always running a control series of specimens of raw stock along with the treated specimens.

The set-up was occasionally readjusted to eliminate the effect of wearing of the holder and changes in speed of the motor. This was done at the beginning of a given series of tests that were

to be mutually comparable, but never in the middle of a series. During any series, the speed of the motor and consequently of the lathe was found to be very nearly constant, but over long periods the latter varied from 1400 to 2000 RPM, depending upon the adjustment of the motor commutator brushes.

B—Testing Strips.

To determine the effect of cleaning and pickling on the strip steel the Erichsen machine (Fig. 2) which is used for testing the

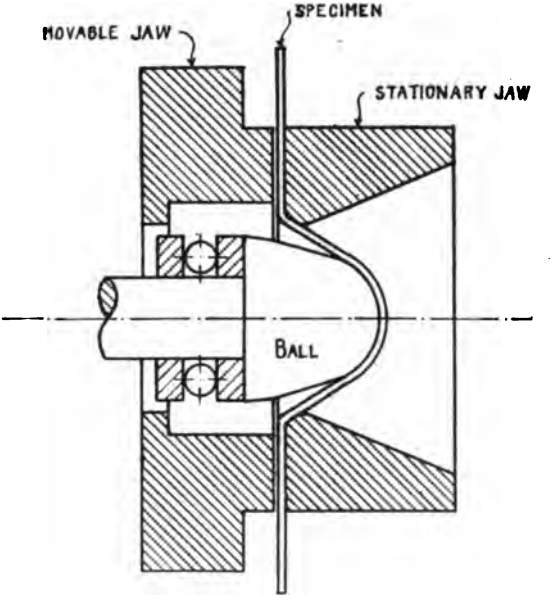

FIG. 2.

"workability" of steel was employed. For this purpose the strip steel was cut into sections 3⅜ inches by 3⅜ inches (8.5 cm. x 8.5 cm.). The specimen when tested was clasped between two dies and held in such a way that the metal had "play" and could flow, while a tool having a rounded end was moved gradually forward under the influence of a ram, actuated by a micrometer screw, until fracture occurred. The depth of impression required to give fracture was read off directly on a micrometer scale graduated to 0.01 mm. (0.0004 in.). In the mechanical details of

testing the practice recommended by the makers of the machine was followed.

Since with both rods and strips of various size, carbon content, heat treatment and amount of cold work, the two methods of testing showed pronounced and in general parallel effects of cleaning and pickling, it is believed that the results of the experiments are at least definite, even if not always quantitative. It should be noted that any slight reduction in cross section produced by the various treatments would of itself cause an apparent decrease in brittleness.

The greatest confidence is to be placed in the data for rods, since the method of test is wholly mechanical and is not subject to personal error. Moreover the percentage effects are usually greater in the case of rods. In order to obtain fracture within reasonably short periods, the degree of eccentricity employed was such as to produce fiber stresses which were, in some cases at least, beyond the elastic limit of the material. In consequence the individual results were probably not so concordant and the percentage reduction in stress periods (*i. e.*, number of stress reversals) was probably not so great as might have been obtained with lower stresses. Since however most of the observed effects were very marked, it is believed that the average results (each of which represent five or more fairly concordant values) indicate the relative effects of the various treatments.

V. METHODS OF EXPRESSING RESULTS.

A—Rods.

The method of expressing results upon the rods was to calculate the percentage reduction of the stress period of the treated specimens as compared with that for the raw stock. Since in any given series of tests the speed of the motor was constant, these periods are proportional to the actual number of stress reversals, and are more convenient to express than the larger and more cumbersome figures for the number of reversals. Since moreover all conclusions are based upon percentage changes as compared with standard material similarly treated, the ultimate results are the same, whichever method of expression is employed. Thus six specimens of raw stock No. 3, 0.31 percent carbon, ⅛ in.

(3.2 mm.) diameter, gave as the times required to break: 67, 52, 76, 74, 72, and 64 seconds, while six similar specimens which were cleaned and pickled in sulphuric acid required: 40, 50, 35, 36, 33, and 42 seconds to break. The raw and pickled specimens were alternately tested. The mean value for the raw stock was 67.5 seconds and for the pickled specimens 39.3 seconds; thus the treatment effected a reduction of 42 percent in the stress period. In addition to illustrating the method of expressing results these figures give an idea as to the consistency of results and the range of variation. The figures for rods of greater diameter do not show so much variation except in the case of high carbon steel, where the range is slightly greater, especially in the case of the hardened and tempered high carbon steels.

In all cases the measurements given are the mean of the values obtained for a group of five or more specimens which had been given identical treatment. In order that a given series of tests would be more nearly comparable among themselves, as far as uniformly representative stock was concerned, they were selected systematically from different portions of the whole strip or rod.

B—Strips.

The method of expressing results for strips was to calculate the percentage reduction of the penetration of the treated specimens as compared with that for the raw stock. Thus five specimens of raw stock F (½ hard 0.0263 in. (0.64 mm.) thick) gave penetrations of 8.60, 8.45, 8.20, 8.35, and 8.50 millimeters, while five similar specimens cleaned and then pickled in sulphuric acid gave 6.60, 6.90, 6.00, 6.30 and 5.95 millimeters penetration respectively. The mean value for the raw stock was 8.4 mm. (0.33 in.) and for the pickled specimens, 6.2 mm. (0.24 in.). Thus there was a reduction in penetration of 2.2 mm. (0.09 in.), *i. e.*, a lowering of the penetration by 26 percent as compared with the raw stock.

VI. THE EFFECT OF CLEANING.

Preparatory to any pickling or finishing operation upon metal, it is usually necessary to remove grease from the surface. In general this operation is designated as "cleaning," as distinguished from removal of oxide or scale by pickling or mechanical pro-

cesses. Commercially, cleaning from grease is usually accomplished by means of organic solvents, or more frequently of alkaline solutions. In the latter case, cleaning is often facilitated by hand scrubbing, using in some cases a mild abrasive such as pumice.

Even though it was not anticipated that the usual cleaning processes would exert any appreciable effect upon the mechanical properties of the steel, it was necessary to investigate their possible effects, in order to permit the selection of such methods or conditions of cleaning as would afford a uniform surface for subsequent pickling experiments. As a matter of fact it was found that ordinary cleaning operations with organic solvents or alkaline solutions may produce an effect upon the results obtained in the testing of strips; and the use of pumice or similar abrasives may produce an appreciable effect upon both rods and strips.

The alkali cleaner used in these investigations consisted of a solution containing 80 grams per liter (10.7 oz./gal.) of sodium carbonate, 20 grams per liter (2.7 oz./gal.) of sodium hydroxide, and 1 gram per liter (0.13 oz./gal.) of rosin. In general the objects were immersed for five minutes in this solution, which was maintained at a temperature of about 70° C. (158° F.). Gasoline and ether were employed in some of the tests, as typical organic solvents such as might be employed for the removal of grease.

No appreciable effect, as measured by the alternating stress test, was produced upon rods by the removal of grease by means of alkali or organic solvents. Electrolytic cleaning, in which the rods were made cathodes in this alkaline solution, with a current density of 3 amp./dm^2, (28 amp./sq. ft.) produced no measurable brittleness, even though there was a vigorous evolution of hydrogen upon the surface. In the case of strips, however, as shown in Table III, the removal of grease by the above methods produced a measurable effect upon the results obtained in the Erichsen test, equivalent to a reduction of from 6 to 9 percent in the penetration values.

The cause of the reduction of penetration of strip steel was not definitely ascertained. It was suggested that the grease lubricates the contact areas between the strip and the testing machine so that there is less friction when the metal surfaces slide over

each other as the strip yields and cracks while under tension. If this were the case, re-greasing the surface should cause complete and immediate recovery. Re-greasing in some instances did cause partial recovery while in some cases recovery became complete after the re-greased specimens had been heated in the oven for 1 hour at 150° C. (302° F.). Complete recovery did not occur in all cases however.

When the grease, and along with it part of the scale on the rods, was removed by vigorous scrubbing with pumice and a brush moistened either with water or with the alkali cleaning solution, there was a reduction in the stress period of from 2 to 15 percent (Table IV).

TABLE III.

Effect of Cleaning Upon Strip Steel F.

Treatment	Penetration		Reduction in Penetration		
	Mm.	In.	Mm.	In.	Per-cent
Raw Stock	9.0	0.35			
Gasoline—10 min.	8.2	0.32	0.8	0.03	9
Ether—10 min.	8.5	0.33	0.5	0.02	6
Alkali—5 min.	8.5	0.33	0.5	0.02	6
Gasoline—5 min. Ether—1 min. Alkali—5 min.	8.2	0.32	0.8	0.03	9

With a variable operation, such as hand scrubbing, it is not reasonable to expect any more uniform or consistent results than are shown in Table IV. It is believed, however, that these effects, even though variable, represent an actual decrease in the ability of the rods to withstand alternating stress. Such an effect can probably be accounted for by the formation of surface scratches.

Vigorous scrubbing with pumice produces an effect upon strip steel of the same magnitude as upon rods, except that the results are still less uniform. This is to be expected, since the scrubbing serves both to remove the grease (which, as previously shown, affects the penetration values) and also to produce scratches upon the surface.

In view of these variable effects of pumice brushing, it was not expedient to include it in the treatment preparatory to pickling or

plating. The following method of cleaning, which was found to give uniformly clean surfaces for pickling, was adopted as the standard practice in all the experiments subsequently conducted. The plates or rods were immersed in gasoline for 5 to 10 minutes, and were then dipped momentarily in ether, which evaporated quickly. They were next placed in the alkali cleaner for about two minutes, after which they were mopped with a wad of cotton saturated with the alkali solution. After three minutes additional immersion in the alkali, they were rinsed. In some of the early

TABLE IV.

Effect of Pumice Scrubbing Upon Rods.

Material			Carbon Per-cent	Treatment	Stress Period	
Stock No.	Diam.				Seconds	Percentage Reduction
	Mm.	In.				
1	9.5	3/8	0.30	none	234	
				Pumice	206	12
2	4.8	3/16	0.33	none	127	
				Pumice	114	10
3	3.2	1/8	0.31	none	50	
				Pumice	49	2
5	4.8	3/16	0.08	none	108	
				Pumice	103	5
6	4.8	3/16	0.54	none	120	
				Pumice—transverse	102	15
				Pumice—longitudinal	107	10

experiments on rods, a very light brushing with pumice was found necessary to furnish a surface which would be uniformly attacked by acid. It is not believed, however, that in these cases the above noted effects of pumice were sufficient to affect the magnitude of the results obtained. In general the percentage decrease in penetration of strips, caused by pickling, was computed from the values of specimens which had been cleaned in the above way and not from the values of the raw stock.

VII. THE EFFECT OF SAND BLASTING.

Although in some cases sand blasting serves the double purpose of removing grease and oxide scale, its primary object is to remove scale. By the use of sand blasting, metal surfaces can be

prepared for plating without the use of chemical pickling agents. This method then should avoid any embrittling effects inherently due to the chemical action of the pickling acid, which effects are commonly supposed to be caused by the presence of hydrogen in some form. On the other hand, as the subsequent data will show,

TABLE V.

Effect of Sand Blasting Upon Rods.

Expt.	Material		Diam		Treatment	Stress Period Seconds	Percentage Effect
	Stock No.	Per-Cent Carbon	In.	Mm.			
A	5	0.08	3/16	4.8	Raw Stock	51	
					Sand Blasted	30	—41
B	2	0.33	3/16	4.8	Raw Stock	56	
					Sand Blasted	33	—41
C	6	0.54	3/16	4.8	Raw Stock	55	
					Sand Blasted	31	—43
D	7	0.89	3/16	4.8	Raw Stock	58	
					Sand Blasted	52	—10
E	7	0.89	3/16	4.8	Hardened and Tempered[1]	141	
					Hardened and Tempered then Sand Blasted	183	+28
F	7	0.89	3/16	4.8	Normalized[2]	89	
					Normalized then Sand Blasted	70	—21
G	1	0.30	3/8	9.5	Raw Stock	236	
					Sand Blasted then heated 4 days at 150°	160	—30
					Heated 4 days then Sand Blasted	163	—31
					Sand Blasted and tested at once	166	—33

[1] Rods hardened by being heated to 800° C. (1,472° F.) and held for three hours, then oil quenched. Tempered by being held for one hour at 400° C. (752° F.) and then air cooled.

[2] Normalized by being heated to 800° C. (1,472° F.) and held for three hours, then air cooled.

the sand blasting itself has a permanent effect on the mechanical properties of some steels, which effect is of the same order of magnitude as that produced by pickling.

In the experiments here described, the attempt was made to make the sand blasting as uniform as possible by blasting all rods of a given set together and using the same quantity of sand for each set. The agreement between individual specimens was

very good. The effect of sand blasting on "raw stock" of the same diameter but different carbon contents is shown in Table V, (experiments A, B, C, and D), where it is evident that for carbon contents up to 0.54 percent the effect is very large, reducing the ability to withstand stress by over 40 percent, while for 0.89 percent carbon steel the effect is only 10 percent. In sharp contrast to this is the case of the high carbon steel rods (experiment E) that had been hardened and tempered. These, instead of being weakened by the sand blasting, were actually able to withstand the alternating stress for a period 28 percent longer than the unblasted rods. On the contrary, sand blasting of normalized high carbon rods (experiment F) produced a reduction in stress period.

TABLE VI.

Effect of Sand Blasting Upon Strips.

Stock Letter	Thickness of Stock		Temper	Penetration				Percentage Reduction in Penetration
				Raw Stock		Sand Blasted		
	In.	Mm.		Mm.	In.	Mm.	In.	
E	0.0253	0.64	Dead soft	10.7	0.42	9.4	0.37	12
F	0.0253	0.64	¼ Hard	9.5	0.37	9.0	0.35	5
F	0.0253	0.64	¼ Hard	9.5	0.37	8.5	0.33	11*
G	0.0253	0.64	Hard	4.8	0.19	4.7	0.18	2

* Double the regular amount of sand was used.

Sand blasting batters off the surface layer, thus very slightly reducing the cross sectional area and roughening the surface. At the same time the blows of the sand particles cause a certain amount of flow of the metal at the surface. This would amount at least to a slight cold work effect on the outer layers of the metal.

The reduction of cross section is practically negligible, but the roughening and possibly the surface cold work tend to cause reduction of stress period, since the surface is both rough and may be more brittle. If this is the case, these effects would be less for hardened steel, as was found by experiment.

That the effect of sand blasting is a permanent one (*i. e.*, is not removed by standing at ordinary temperatures or by heating to

slightly elevated temperatures) is shown by data given under Experiment G, Table V. The steel rods which were sand blasted and tested at once gave the same reduction in stress period as those sand blasted and heated four days at 150° C. (302° F.) before testing.

Sand blasting of strip steel (see Table VI) causes slight reduction in penetration for the dead soft and quarter hard stock. The hard stock, which had been subjected to very severe cold work (see Table II), was affected very slightly if at all.

When strip steel was sand blasted on one side the area of that side was increased and this caused the strip to bend and assume a curved surface convex on the blasted side. On turning the strip over and sand blasting the other side the curvature was counteracted.

Practically no loss in weight of strip steel was produced by sand blasting. Apparently the gain in weight produced by sand particles becoming imbedded in the surface about compensated for any slight loss in weight of the metal. Measurements of the thickness made with a micrometer caliper were rendered uncertain by the roughening of the surface produced by the sand blasting. It is, however, certain that any dimensional changes are not great enough to account for the observed change in mechanical properties. It would seem that the cold work of sand blasting is responsible for the decrease in the fatigue properties of the rods and in the workability of the sheets. Hardening due to cold work offers the simplest explanation for both effects.

Attention is called to the unexpected fact that sand blasting caused an increase in the stress period of the hardened rods, instead of a decrease as with all others. Evidence as to the cause of this phenomenon is lacking, but a surmise could attribute it to a favorable change in the molecular arrangement or molecular equilibrium of the steel at the surface, possibly in connection with a transitory molecular liquefaction, as hypothesized by Beilby[28] for all cold work. The true explanation, which can be arrived at only after considerable research, may involve initial stresses in these particular rods, or surface roughening by oxidation in the heat treatment, or the initial arrangement of the structural constituents of the steel.

[28] "Hard and Soft State in Metals." Journ Inst. of Metals (1911), 4, No. 2.

VIII. THE EFFECT OF PICKLING.

A. General Effects of Sulphuric Acid Pickling.

For the removal of oxide scale from steel the most common practice is to immerse in an acid bath. The scale is in part dissolved and in part torn off mechanically by the hydrogen formed by the action of the acid on the metal. The acids commonly used which are considered in this work are sulphuric acid, sodium acid sulphate or nitre cake, hydrochloric acid, hydrofluoric acid, and nitric acid. In order that the results would be nearly comparable, twice normal solutions (in terms of available hydrogen) were used in all cases unless otherwise specifically stated. This concentration was arbitrarily chosen, but it had the advantage of giving pickling baths which were of definite composition and which were chemically equivalent although not of the same actual hydrogen ion content. Furthermore, twice normal solutions are of approximately the same concentration as those frequently used in actual practice. For example, the sulphuric acid bath was almost 10 percent, and the hydrofluoric acid about 4 percent.

As a reference for comparison, a "standard" pickling process was adopted. This consisted of immersion in 2 *N*. H_2SO_4 at 50° C. (122° F.) for five minutes. These conditions were selected as a result of preliminary experiments which showed that this treatment was vigorous enough to produce pronounced solvent action upon oxides, while the actual loss of metal by solution was very slight (less than 0.5 percent by weight for $\frac{1}{8}$ in. (3.2 mm.) steel rods). This method of pickling is not advocated, but was adopted solely to enable comparative results to be obtained.

In Table VII is given a summary showing the percentage reduction in stress period produced by the sulphuric acid pickle on $\frac{3}{16}$ in. (4.8 mm.) rods of various carbon contents and treatments. The "raw" stock was given the standard pickle. The heat-treated specimens were given twice as long an immersion, which was necessary on account of the adhering scale which slowed up the pickling action.

The data in Table VII show clearly that pickling in sulphuric acid produces a very marked reduction in the ability of the steel rods to withstand stress. For rods which were not heat treated, (*i. e.*, the raw stock as received), the effect is least for the high

carbon steel. For the normalized stock the effect of pickling decreases as the carbon content increases, while the reverse is true for the hardened and tempered rods. The behavior of the very high carbon steel (0.89 percent) is especially interesting. The figures given show 60 to 100 percent reduction in stress period produced by pickling. The 100 percent figure refers to specimens that broke at once when the stressing was started, which was generally the case for the hardest of the heat treated specimens. It should be recognized that if a lower stress were applied in any given series the stress periods would be greater and might even assume a different relative order. The results for high carbon steel were not nearly so uniform as in the case of the lower carbon content, but they were so pronounced that there is no doubt that they represent a real effect.

TABLE VII.

Effect of Sulphuric Acid Pickling on $\frac{3}{16}$" (4.8 mm.) Rods.

Alternating Stress Test.

Stock Number	5	2	6	7
Carbon content, percent.	0.08	0.33	0.54	0.89
Stock as received. Stress period—seconds	40	55	56	15
Normalized. Reduction in stress period—percent	30	42	10	3
Hardened and tempered. Reduction in stress period—percent	7	26	28	50 to 100

The heat treatment given the rods for which data are shown in Table VII was as follows: The rods, which had been wired in bundles of twelve, were suspended in a crucible and the bundles separated by, and covered with, asbestos, which tended to decrease oxidation. The packed crucible was placed in an electric muffle furnace which was gradually brought to about 800° C. (1472° F.). Different batches of the same carbon content were given identical treatment, and the specimens to be normalized were taken from the furnace and air cooled. Those to be hardened were quenched in oil and later tempered by being heated in a packed crucible as above for 1 hour at 240° C. (464° F.) in the muffle furnace and then cooled in air. The thin coat of scale which had been formed was broken and partly removed by subjecting the heat-treated

rods to mild tumbling for 3½ hours. Otherwise large flakes of scale might have prevented uniform action of the pickling acid.

Application of the "standard" pickling process to rods of different sizes but approximately the same carbon content, yielded rather remarkable results. Thus it was found that with ⅜ in. (9.5 mm.) rods (stock No. 1) and $\frac{3}{16}$ in. (4.8 mm.) rods (stock No. 4) the reduction in stress period was from 30 to 60 percent, *i. e.*, actually slightly greater than with ⅛ in. (3.2 mm.) rods (stock No. 3), for which the reduction in stress period was 20 to 50 percent. It is very striking to observe that pickling of rods ⅜ in. (9.5 mm.) in diameter for 5 minutes in approximately 10 percent sulphuric acid, should reduce the ability to withstand alternating stress (under the conditions used) by 50 percent or more.

TABLE VIII.

Effect of "Standard" Pickle on Strip Steel.

Erichsen Penetration

Stock Letter	Temper	Thickness		Raw Stock Penetration		Cleaned and Pickled Penetration		Reduction in Penetration		
		In.	Mm.	Mm.	In.	Mm.	In.	Mm.	In.	%
A	Dead	0.0126	0.320	10.5	0.41	9.55	0.376	0.95	0.037	9
E	Soft	0.0253	0.643	10.1	0.40	9.5	0.374	0.6	0.0236	6
H		0.0358	0.909	10.9	0.43	10.4	0.409	0.5	0.0197	5
B		0.0126	0.320	6.0	0.24	5.5	0.216	0.5	0.0197	8
F	¼ Hard	0.0253	0.643	9.2	0.36	7.3	0.287	1.9	0.07	20
I		0.0358	0.909	8.8	0.35	7.1	0.279	1.6	0.06	18
C	½ Hard	0.0126	0.320	5.9	0.23	4.3	0.17	1.6	0.06	27
D		0.0126	0.320	4.5	0.18	3.4	0.13	1.1	0.04	24
G	Hard	0.0253	0.643	4.2	0.16	2.4	0.09	1.8	0.07	43
J		0.0358	0.909	5.8	0.22	3.0	0.11	2.8	0.11	48

With strip steel, the percentage reduction of penetration caused by pickling shows marked variation with different thicknesses and different grades of hardness. (See Table VIII).

In general the reduction in penetration was greater the harder the stock. It will be noticed that as the hardness (amount of cold work) increased, there was a decrease in the actual amount of penetration, and an increase in the percentage effect of the

pickling. The latter data should be considered when comparing different grades of stock, since the difference in the actual penetration is not always significant. The ductility of the thick strips was more reduced by pickling than was that of the thinner stock.

B. The Temperature and Time of Pickling.

Since sulphuric acid is one of the commonest pickling baths, it was used to determine the effect of the temperature and the duration of the pickling. The data for the influence of temperature are given in Table IX where it is clearly shown that up to about 50° C. (122° F.) increase in temperature causes an increased effect of pickling.

TABLE IX.

Influence of Temperature Upon Effect of Pickling.

(5 min. in 2 N. H_2SO_4.)

Temp. of Pickling Bath °C.	°F.	Reduction in Stress Period, ¼ inch (1.2 mm.), Rods (No. 1), Percent	Reduction in Penetration, Strip Steel F, Percent
0	32	8	6
20	68	14	13
30	86	9	15
40	104	16	15
50	122	29	19
80	176	33	15
100	212	27	14

The effect of the length of immersion for a given temperature is shown in Table X, where it is made evident that the brittleness increases rapidly at first and then more gradually after the first 5 or 10 minutes.

TABLE X.

Influence of Duration of Pickling

(In 2 N. H_2SO_4 at 50° C.)

Pickling Period, Min.	Reduction in Stress Period, ¼ inch (1.2 mm.), Rods (No. 1), Percent	Reduction in Penetration, Strip Steel F, Percent
[illegible]	1	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
30	[illegible]	[illegible]

The above figures for the effect of time and temperature show that the choice of conditions for the "standard pickle" was fully justified, since 5 minutes at 50° C. (122° F.) produces nearly the maximum effect, with the minimum opportunity for solution of the metal.

C. Pickling in Various Acid Solutions.

1. *Niter Cake* ($NaHSO_4$). The experiments showed that niter cake, which is extensively used as a substitute for sulphuric acid, produces about the same brittleness effects in steel as does sulphuric acid of the same acid normality. It was found, however, that a solution of niter cake 2 *N* in $NaHSO_4$ requires a higher temperature to produce satisfactory pickling than does sulphuric acid of equivalent strength. The solution was therefore used at nearly the boiling temperature.

Under these conditions the steel rods (stock No. 4) when immersed for 5 minutes suffered a reduction in the alternating stress period of 39 percent. Similarly strip steel (stock F) showed a reduction in penetration of 21 percent after 5 minutes' immersion and 24 percent after 10 minutes' immersion. Results obtained with chemically pure sodium sulphate were practically the same as with niter cake.

2. *Hydrofluoric Acid.* Hydrofluoric acid, which is used especially where silica is to be removed, as in the case of castings and sand blasted articles, produces a marked embrittlement in steel. Thus upon immersion in 2 *N* hydrofluoric acid at 30° C. (86° F.) for 30 minutes, rods (stock No. 2) showed a reduction in stress period of 36 percent; rods (stock No. 1) which were first sand blasted and then pickled in hydrofluoric acid were reduced in stress period by 74 percent (of which 16 percent represents the effect of sand blasting).

Similarly strip steel (stock F) when pickled in hydrofluoric acid for 5 minutes at 30° C. (86° F.) had its penetration reduced 13 percent, and when pickled 30 minutes, the reduction was 15 percent.

These results are of special interest, since at room temperature (in this case 30° C. or 86° F.) the hydrofluoric acid acts so

slowly upon the steel that there is little visible evolution of hydrogen.

3. *Hydrochloric Acid.* With hydrochloric acid the effects upon rods were very nearly the same as with the "standard" sulphuric acid pickling. Immersion in 2 *N* or in concentrated hydrochloric acid for 5 minutes at 35° C. (95° F.) produced about the same reduction in stress period, *i. e.*, 26 percent. Similarly hydrochloric acid produced about the same effect on strip steel as did the sulphuric acid.

4. *Nitric Acid.* With nitric acid practically no reduction in the stress period of rods was produced, and but a slight reduction (about 7 percent) in the penetration value of strips. In these experiments it was necessary to exercise care to prevent too rapid action of the dilute nitric acid, which would thereby produce great reduction in cross section. With concentrated nitric acid the initial rapid action was followed by passivity. It is probable that what slight effect was observed with strips was due to roughening of the surface, rather than to actual brittleness.

D. Electrolytic Pickling.

As shown in Table XI, electrolytic pickling in 2 *N* sulphuric acid produced slightly greater brittleness than simple immersion pickling of the same duration, regardless of whether the steel was used as the anode or as the cathode. When the cathode treatment was followed by a brief reversal of polarity no reduction of brittleness was accomplished. Owing to changes in polarization the voltage between the plates was variable but in no case exceeded 0.8 volt.

Alternating current pickling in 2 *N* H_2SO_4 at 25° C. (77° F.) produced about the same brittleness as that caused by anode or cathode pickling regardless of whether the current density was 0.6 or 3.0 amp./dm.^{2} (5.6 or 28 amp./sq. ft.).

To eliminate the simultaneous pickling action due to the mere immersion in the acid, a series of steel plates was subjected to electrolysis, some as cathodes and some as anodes, in sodium sulphate solution (2 *N* Na_2SO_4). Very little if any brittleness was produced, although on the plates used as cathode there was a vigorous evolution of hydrogen.

TABLE XI.

Effect of Electrolytic Pickling.

In 2 *N* H_2SO_4 at 25° C. (77° F.)

Electrode	Current Density		Time Min.	Rods Stock No. 6 Reduction in Stress Period Percent	Strips Stock F Reduction in Penetration Percent
	Amp./dm.²	Amp./sq. ft.			
Anode	2	18.6	1	2	..
Anode	2	18.6	2 ..	30	..
Anode	2	18.6	5	39	..
Cathode	2	18.6	5	32	..
Cathode	2	18.6	5	..	..
+Anode	..	..	0.5	45	..
Anode	1.3	12.1	1	..	18
Anode	1.3	12.1	3	..	24
Cathode	1.3	12.1	5	..	29.
Cathode	1.3	12.1	5	..	
+Anode			0.5	..	26

IX. TREATMENT AFTER PICKLING.

In view of the relatively great brittleness produced in both steel rods and strips by the ordinary pickling operations, it becomes important to determine by what means such brittleness may be reduced or eliminated. If, as is generally admitted, the embrittling effects are due to or connected with the occlusion of hydrogen, any treatment which will facilitate the removal or expulsion of such occluded hydrogen should in some degree reduce the brittleness. Among the conditions which might be favorable to the removal of the hydrogen and consequently of the brittleness are (*a*) standing at ordinary temperatures, (*b*) exposure to elevated temperatures, and (*c*) treatment with oxidizing agents.

A. Effect of Standing.

In order to determine what change in brittleness occurs in pickled steel when the latter is allowed to stand at ordinary temperature, a large number of plates of strip steel (stock F) were

given the usual cleaning and pickled in the "standard" sulphuric acid, after which they were carefully rinsed and dried. In Table XII are given the average results obtained by tests of from 3 to 6 of these specimens at various intervals.

TABLE XII.

Effect of Standing Upon Brittleness. Strip Steel F.
Standard Pickle.

Interval Between Pickling and Testing		Penetration		Decrease in Penetration Percent
Days	Hrs.	Mm.	In.	
(Cleaned But Not Pickled)		(8.1)	(0.32)	
..	0	6.6	0.26	16
..	1	6.3	0.25	22
..	19	6.6	0.26	18
1	1	7.0	0.276	14
1	19	7.1	0.280	12
2	2	7.3	0.287	10
3	..	7.5	0.295	7
4	..	7.4	0.291	9
6	..	7.7	0.303	5
7	..	7.7	0.303	5
11	..	7.4	0.291	9
15	..	7.5	0.295	7
34	..	7.3	0.287	10

From the results in Table XII it may be seen that upon standing, there is a gradual decrease in brittleness (*i. e.*, a decrease in the percentage reduction in penetration) up to about 3 days, after which the results remain nearly constant. (The low penetration of the specimens tested after 34 days standing may have been due to slight rusting which occurred upon them). It should be noted that even after long standing, the original ductility was not entirely restored.

With pickled steel rods it was found that upon standing there was a similar recovery, as measured by the alternating stress test, and that in general this recovery was more nearly complete than with plates.

B. Effect of Heating.

When steel plates which had been cleaned and pickled under the "standard" conditions, were heated in an air oven to 100° C. (212° F.) a more rapid recovery of ductility occurred, as shown in Table XIII. The maximum recovery occurred within 2 hours. In no case, however, was the original ductility restored.

TABLE XIII.

Effect of Heating Upon Brittleness—Strip Steel F.
Standard Pickle. Heated to 100° C. in Air Oven.

Duration of Heating.		Penetration		Decrease in Penetration Percent
Days	Hrs.	Mm.	In.	
(Cleaned But Not Pickled)		(8.1)	(0.32)	
..	0	5.8	0.228	28
..	0.5	6.7	0.264	17
..	1	7.1	0.280	12
..	2	7.8	0.307	4
..	3	7.6	0.299	6
..	5	7.6	0.299	6
..	17	7.6	0.299	6
2	17	7.8	0.307	4
8	..	7.5	0.295	7
11	..	7.7	0.303	5

With steel rods, similar results were obtained at 100° C. (212° F.). By increasing the temperature to 150° C. (302° F.) it was found that the maximum recovery occurred within 10 minutes; but when the temperature was increased to 200° C. (392° F.) no measurable increase in the rate of recovery was observed.

If, instead of heating in an air oven to 100° C. (212° F.), the previously pickled rods or plates are immersed in boiling water, recovery is much more rapid. Thus it was found that with ½ in. (3.2 mm.) rods, a reduction in stress period of 30 percent, caused by pickling, was reduced to 15 percent by 2 minutes' immersion in boiling water, and to 8 percent by 10 minutes' immersion. Strip steel, similarly treated, showed nearly the maximum recovery after only 5 minutes' immersion in boiling water. In general, the

strip steel which was most affected by pickling showed the most rapid recovery upon treatment with boiling water. Neither the thickness of the plates or the diameter of the rods had any measurable effect upon the rate of restoration by heating. In general it was found that the recovery which occurred on standing or heating was practically the same, whether the steel had been pickled in the standard sulphuric acid, sodium acid sulphate, hydrochloric or hydrofluoric acid. The behavior was quite different however with steel that had been pickled in nitric acid. It will be recalled (page 567) that the effects of such pickling were in general slight, and were probably attributable to roughening of the surface rather than to internal embrittlement. This view is substantiated by the fact that upon heating strip steel which had been previously pickled in nitric acid to 150° C. (302° F.), there was no change in penetration. It is also significant that the penetration value of strip steel which had been pickled in nitric acid (whether subsequently heated or not) is almost identical with that of the same steel treated with sulphuric acid and subsequently heated till maximum restoration occurs.

Consideration of these facts indicates clearly that the effect of such an acid as sulphuric acid really consists of two separate but superimposed effects: (1) an etching or roughening of the surface, the influence of which is not removed by heating, and (2) an absorption of hydrogen, the embrittling effect of which is eliminated by heating or long standing. These may therefore be designated respectively as the permanent and the temporary effects of pickling.

C. Effect of Oxidizing Agents.

If the temporary brittleness, as above defined, is due to occlusion of hydrogen, it is at least conceivable that by the action of suitable oxidizing agents its effect might be reduced or eliminated. Thus it has been claimed by commercial platers that an immersion in nitric acid after the usual pickling operation eliminates brittleness. This observation could not however be confirmed by the authors. Neither immersion in 2 *N* nitric acid for two minutes, nor in concentrated nitric acid for ten seconds, produced any measurable reduction in the brittleness of rods or strips previously pickled in

sulphuric acid. Longer immersions than these were impracticable since in that case the rapid action of the nitric acid would greatly reduce the thickness of the specimens and thus vitiate the results. It appeared to make no difference in these experiments whether the steel was active or passive in the nitric acid. Similarly it was found that immersion in molar potassium dichromate solution, a powerful oxidizing agent, exerted no measurable effect upon the brittleness.

The failure of oxidizing agents under these conditions to reduce the brittleness is not valid evidence against the assumption that the brittleness is due to the presence of hydrogen. Even though, as recently shown by Fuller,[24] penetration of hydrogen through steel is relatively rapid, the diffusion of the occluded hydrogen may be so slow (as indeed is indicated by the experiments upon standing at room temperature) as to prevent rapid action of any oxidizing agent. Or, as is very probable, the occluded hydrogen may be in the molecular state, and not therefore readily susceptible to oxidation.

It may also be mentioned that treatment of pickled steel with sodium or ammonium hydroxide solution produced no change in the brittleness. This point is of interest as indicating that the brittleness produced by pickling is not, as is popularly supposed, due to absorption of the pickling acid. Wherever neutralization after pickling is found beneficial, it is because it prevents further corrosion by any acid that might be present in cracks or crevices in the steel.

X. SUMMARY.

The results obtained in this investigation may be summarized as follows. These effects were obtained by measuring the brittleness of plain carbon steel rods by the alternating stress method and of plates by the Erichsen penetration method. They do not necessarily apply, quantitatively at least, to other methods or conditions (*e. g.*, other values or rates of alternation of the stress) which may be employed for testing the brittleness of steel, or to special alloy steels. In view, however, of the large magnitude of many of the observed effects, it is probable that they are of general application.

[24] Trans. Amer. Electrochem. Soc. (1919), **36**, 113.

A. Cleaning.

1. The strength of rods is practically unaffected by the removal of grease, either by means of organic solvents or by immersion in alkali.

2. The removal of grease from plates causes a reduction of about 10 percent in the penetration values. That this change is probably due to a change in the surface condition rather than to an actual change in the physical properties of the steel, is indicated by the fact that the penetration value in certain instances approaches the original if the plates are regreased, especially if after regreasing they are slightly heated.

3. Vigorous pumice brushing causes a reduction in strength of both rods and plates. This effect is obviously due to the scratching of the surface by the pumice.

4. Electrolytic cleaning (as cathode) of rods or plates in the alkali cleaner does not produce any greater change than is caused by simple immersion in alkali.

B. Sand Blasting.

1. Sand blasting of steel rods in the "raw" state and also those which have been normalized, causes appreciable reduction in ability to withstand the alternating stress test. This effect is most marked with steel of relatively low or medium carbon content, *e. g.*, up to 0.54 percent, for which the reduction is about 40 percent. For high carbon steel, *e. g.*, 0.89 percent, the effect is only about 10 percent. The effects are about the same upon $\frac{3}{16}$ in. (4.8 mm.) as upon $\frac{3}{8}$ in. (9.5 mm.) rods.

2. If high carbon steel (*e. g.*, 0.98 percent) that has been hardened and tempered is sand blasted, it is actually rendered more capable of withstanding alternating stress.

3. Cold-rolled strip steel is only slightly reduced in ductility by sand blasting.

C. Pickling.

1. Pickling under "standard" conditions, *i. e.*, 5 minutes in 2 *N* sulphuric acid at 50° C. (122° F.) produces the following effects on rods:

(*a*) The stock as received is rendered increasingly brittle with increasing carbon content up to about 0.54 percent carbon. The brittleness produced in the high carbon steel is less marked.

(*b*) The brittleness produced in normalized steel rods decreases with increasing carbon content.

(*c*) The brittleness produced in hardened and tempered steel rods increases with increasing carbon content.

(*d*) These effects on rods were almost independent of size from ⅛ inch (3.2 mm.) to ⅜ in. (9.5 mm.) in diameter.

2. The "standard" pickling produced the following effects upon cold-rolled strip steel.

(*a*) The brittleness caused by pickling is greatest for steel that is "hardest," *i. e.*, has received the greatest amount of cold work in its final stages of manufacture.

(*b*) Within the limits tested, the brittleness caused by pickling increases with the thickness of the strips.

3. Increasing the temperature of the pickling bath from 0° C. (32° F.) to 50° C. (122° F.) causes increased brittleness, but above 50° C. (122° F.) increasing the temperature has little effect.

4. The brittleness increases with the time of immersion in the pickling bath. This increase is most marked up to 5 minutes immersion, after which the increase in brittleness is more gradual. Effects produced by long immersion are no doubt due in large part to solution of the metal, and consequently reduction in dimensions.

5. Pickling in sodium acid sulphate (niter cake), hydrochloric acid, or hydrofluoric acid produces practically the same embrittling effects as in sulphuric acid of equivalent acid concentration.

6. Nitric acid produces practically no brittleness in rods. It produces a slight reduction in penetration of strips, caused probably by the etching or roughening of the surface.

7. Electrolytic pickling, whether the steel is made anode or cathode, or is made cathode and then anode, or if alternating current is used, causes about the same degree of brittleness as is produced by simple immersion in the same acid for an equal period of time. No doubt the effects due to immersion occur

simultaneously with the electrolytic pickling, and may mask any minor effects of the latter. Electrolytic "pickling" as anode or cathode in a neutral sodium sulphate solution produced no brittleness, although hydrogen was evolved vigorously upon the cathode surface.

D. Treatment After Pickling.

1. Steel which has been rendered brittle by pickling becomes less brittle upon standing at ordinary temperature. With steel rods this recovery is nearly complete in three days. With steel plates the recovery is never quite complete, but reaches a maximum in about three days.

2. In air, at higher temperatures, the maximum recovery takes place more rapidly, *e. g.,* in about 2 hours at 100° C. (212° F.) and in 10 minutes at 150° C. (302° F). Heating to 200° C. (392° F.) does not appreciably further increase the rate of recovery.

3. When the embrittled steel is heated in water at 100° C. (212° F.), the maximum recovery occurs in from 2 to 5 minutes. The rate of recovery of rods is practically independent of size, up to ⅜ in. (9.5 mm.).

4. Brittleness produced by pickling in sodium acid sulphate, hydrochloric acid, or hydrofluoric acid, is removed under the same conditions as that produced by sulphuric acid. What slight brittleness is caused by pickling in nitric acid is not reduced by heating under any of the above conditions.

5. In no case does strip steel give the original penetration values, even when the maximum restoration has occurred. The final value after pickling and heating is approximately the same as that obtained by nitric acid pickling. It is therefore believed that the effect of pickling consists of;

(*a*) A permanent effect, caused by the roughening of the surface.

(*b*) A temporary effect, due probably to occlusion of hydrogen.

6. Treatment of embrittled steel rods with oxidizing agents, such as nitric acid or potassium dichromate solution, does not produce any measurable decrease in brittleness.

XI. ACKNOWLEDGMENTS.

In conclusion the authors desire to express their appreciation for advice and assistance received from various members of the Bureau staff, especially William Blum, H. R. Yerger, H. E. Haring and A. E. Hummer. We also desire to express our especial indebtedness to the Morris and Bailey Steel Company of Pittsburgh, Pa., and the American Steel & Wire Co., of Worcester, Mass., for preparing the steel required in this investigation.

DISCUSSION.

WILLIAM BLUM[1]: I will present this paper on behalf of the authors, both of whom have left the government service. The work described in this paper is not exhaustive. It was taken up from the standpoint of its relation to electro-plating and the preparation of materials for plating, but the work on the actual effects of plating was not completed at the time it was necessary to discontinue the investigation. Nevertheless it seems desirable to present the rather large amount of empirical data obtained, even though no attempt is made to go into any study of the scientific causes underlying the phenomena. It is interesting to note that the subject of the effect of pickling has always been of a great deal of importance, even though there has been very little accurate information available. During the war the question was brought up repeatedly as to whether pickling or plating operations would affect the properties of steel, such, for example, as those used in airplane construction. Owing to the fact that there was no definite information upon the exact nature or magnitude of these effects, some curious anomalies in practice existed. For example, airplane manufacturers were all willing to admit that zinc plating was a much better form of protection for steel than copper plating as practiced, but they were afraid that zinc plating might produce brittleness. The fact that copper plating might also produce brittleness did not, however, keep them from using the copper plating!

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A. S. CUSHMAN[2]: Everything points to the fact that gases held in one way or another by metals have a decided influence on their critical physical characteristics. For instance, when we "pickle" iron or steel in a dilute acid bath, hydrogen is not only given off in a nascent state, it is also absorbed by the metal and produces an "embrittling" effect. It is possible this absorbed hydrogen is responsible for the pinholes which occur in many forms of coated sheet metals. When iron or steel is annealed in hydrogen gas, we have no "embrittling" but on the contrary the metal is rendered softer and more ductile. Perhaps Dr. Bancroft can give us an explanation of these effects.

G. M. BERRY[3]: I would like to ask the authors of this paper, in connection with their statement that when the test specimen was pickled in nitric acid the brittleness was not removed by subsequent heating, whether, in their opinion, that is due to nitrogen in some form or other being adsorbed.

WILLIAM BLUM: There is no measurable brittleness produced in steel rods by pickling them in nitric acid, whereas with the steel plates we found there was a decrease in penetration, in all cases less than 10 percent, produced by the nitric acid pickling. That decrease we attributed to a roughening of the surface because it was exactly similar to that produced by sand blasting. I do not think it is due to the adsorption of any material from the nitric acid. As mentioned in the paper, it is not possible to overcome the embrittling effects of hydrogen by treatment for short periods with oxidizing agents; showing that the occluded hydrogen is not readily susceptible to the action of oxidizing agents.

G. M. BERRY: I will say one thing more in reference to hydrogen not being absorbed when steel is annealed in an atmosphere of hydrogen. The difference is a matter of temperature. Probably if you took the metal when it had been pickled and heated it to an elevated temperature, the hydrogen would be driven off; in annealing, the hydrogen is expelled in the same way or does not get in at all, and if it is impregnated with hydrogen, the hydrogen is expelled at the higher temperature.

W. D. BANCROFT[4]: I am glad Mr. Berry has pulled me out of the hole I was supposed to be in. If he had not done so, I should

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[3] Chief Chemist, Halcomb Steel Co., Syracuse, N. Y.
[4] Professor of Physical Chemistry, Cornell University.

have pointed out that another effect of heating hydrogen is to give you slightly larger crystals and therefore make the thing softer, so I do not think that hole is more than a mere depression.

A. S. CUSHMAN: I think the reason why hydrogen in annealing operations softens metal is because it reduces dissolved oxides and this produces a softer condition. If Dr. Bancroft's explanation was all there is to hydrogen annealing the same "dead softness" could be produced by heating in any inert atmosphere, which I don't believe is the case. Why hydrogen adsorbed in a pickling operation embrittles the metal, I do not know, and I do not think anybody else knows.

W. D. BANCROFT: Mr. Cushman's explanation may be quite right with regard to iron, but it certainly is not right as regards the annealing of hard-drawn copper wire or bronzes, where the thing is practically exclusively a change to the crystal side. I happen to know about that particular case.

G. M. BERRY: That brings to mind the preface of the book of Dr. C. M. Johnson, of the Crucible Steel Company of America. In the preface to his book, he has a theory introduced that the elements alloyed with iron are valuable or efficacious in relation to their melting points, taking carbon and going down through the series until, with hydrogen, we have one of the most deleterious which exists. This is also my own experience. I know of no exception. Tungsten, for instance, has a very high melting point, and is one of our most efficacious metals.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 10, 1920, President Bancroft in the Chair.

THE EVOLUTION OF THE ELECTRIC BRASS FURNACE.[1]

By H. M. St. John.[2]

ABSTRACT.

The evolution is considered from the standpoint of the survival of the fittest. The furnaces are classified as (1) induction or direct resistance, in which heat is generated by the direct resistance of the metal itself; (2) indirect resistance, in which heat is generated in a resistor and transferred by radiation or conduction to the metal to be heated, and (3) arc furnaces, in which heat is transferred to the metal directly or indirectly by conduction or radiation. The various types of brass melting furnaces are discussed under these three heads. [J. W. R.]

The evolution of the electric brass-melting furnace bears, in many ways, a rather striking resemblance to that progressive development of flora and fauna with which readers of Darwin are familiar. In the beginning—or very soon after the beginning—there existed several furnace species, each species subdivided into a multitude of varieties, all branches of the same parent stem but differing one from another in certain important details. As time went on many of these varieties proved unfit to contend with the necessities of their environment and became extinct. At the same time new varieties were continually making their appearance, prospering for a time, and eventually sharing what appeared to be the universal fate. After a time, however, it became apparent that the laws of Nature were working toward a well-defined end and that the whole process of evolution was based on a general principle which was both universal and pro-

[1] Manuscript received February 9, 1920.

[2] Sales Engineer, Detroit Electric Furnace Company.

gressive. In each species, one or two varieties proved to be more hardy than the others, preserving an existence of sufficient duration to permit of appreciable development in the desired direction. At present it may be said that each species has developed at least one variety capable of a sustained conflict with its fellows of other species in the common struggle for existence.

During the formative stage the most severe competition was between varieties of the same species, each species developing in its own way without much regard to the others. As the natural process of destructive elimination began to thin out the varieties, and those varieties which survived became more and more sturdy and able to take care of themselves, the survivors of the various family warfares began to come into conflict with their neighbors of other species, each striving to prove its right to enjoy the most favored conditions of existence. As might have been expected, one or two of the original species have so far achieved their claim to supremacy that they are at present multiplying like rabbits in the grassy open spaces, where food is plentiful and nutritious, while the less fortunate have taken to the woods and are leading a precarious existence on roots and herbs. Probably this is carrying the analogy far enough.

A comprehensive study of the electric furnace patents which have been issued in the United States leads one into a chaos which might well puzzle Darwin himself. Most of the original ideas were conceived by men who obviously knew very little about the practical requirements of the foundry or brass mill. A large majority of these patents describe furnace structures which never existed except on paper. The bulk of the remainder, which did contain some germ of practicality, bear little resemblance to those furnaces which are now in commercial use. It is possible, however, to classify all of the proposed furnaces into three general classes which are fundamentally different in principle.

An electric furnace classification is based, as a rule, on the difference of method utilized for the application of heat to the material under treatment. In this case the species are three: (1) The induction or direct resistance furnace, in which heat is generated in the metal itself by virtue of its own resistance to the passage of an electric current; (2) The arc furnace, in which heat is generated between an electrode and the metal, or between

independent electrodes, and transferred to the metal by conduction or radiation, direct or indirect; (3) The indirect resistance furnace, in which heat is transferred from an incandescent resistor to the metal by conduction or radiation, somewhat as in the arc furnace. All of the electric furnaces so far proposed for melting brass naturally fall in one of these classes, or a combination of some two of them.

In the beginning the would-be inventor of an electric brass-melting furnace was obsessed by the idea that such a furnace should bear a close resemblance to the combustion furnaces then in use for that purpose. The tendency was much the same as that which caused the early gasoline engine to be installed in a buggy; the horse was eliminated but the whip socket continued to be used for some time. The clay-graphite crucible, or something closely resembling it in form and composition, was considered essential.

In the electric crucible furnace, as in the fuel-fired crucible furnace, the heat must, in general, be generated at some point outside the crucible and transmitted to the metal through its walls. A favorite suggestion was to surround the crucible with an electric resistor of granular nature, which was heated to incandescence by the passage through it of a suitable electric current. The well-known vagaries of the carbonaceous granular resistor usually proved to be a fatal stumbling block. The resistor developed hot spots so high in temperature that the neighboring refractories were destroyed; the crucible walls were excellent conductors at high temperatures and carried much of the current, with a resulting partial short-circuit through the metal within the crucible; the electrical contact between the granular resistor and the crucible was not of the best and the resultant arcs invariably destroyed the crucible in a very short time.

Most of these fundamental difficulties were obviated by using a resistor which surrounded the crucible but did not come in contact with it. In this way the heat generated in the resistor was first transmitted to the crucible by radiation, and, finally, by conduction through the walls of the crucible to the metal. The great difficulty here was to develop a resistor sufficiently refractory to withstand the high temperatures required, and at the same time possessing electrical characteristics which would permit the

generation of a uniform, controllable heat. The granular resistor had not yet been tamed and was found unsuitable. Molded mixtures of carbon with refractory materials of higher electrical resistance disintegrated in a relatively short time at the high temperature required. Pure carbon or graphite were low in resistance and required the use of an excessive current at a low voltage. The use of carbon or graphite also made necessary resistance elements of small cross-section, in order that the electrical resistance might be as high as possible, and these were rapidly consumed by such oxygen as unavoidably found its way into the furnace chamber. Carborundum, with its faculty for suddenly changing from an excellent insulator to a conductor of comparatively low resistance, was found to be electrically unsuitable.

To the writer's knowledge, the only furnace of this type which was ever operated with any degree of technical success was equipped with wall resistors of thin carbon slabs, provided with means of variably adjusting the contact pressure between the slabs. The generation of heat in this furnace depended, not on the resistance of the carbon itself, but on the contact resistance between the slabs, which could be varied at will in such a way as to provide an excellent means of controlling the current and voltage, and thus the rate of power input. While the oxidation of carbon parts was sufficiently rapid to make the cost of their replacement a serious matter, they were durable enough to permit steady and reliable operation of the furnace for considerable periods. The rate of melting was rapid, considering that the capacity of the furnace was only about 200 pounds, the metal losses were very low, and the quality of metal produced was excellent.

Despite its good qualities, it was soon apparent that this furnace could never be commercially successful. Its maintenance cost, both for carbon electrical parts and refractories, was a serious handicap, but more serious still was the fact that its thermal efficiency was inherently and irremediably low. The fact that the furnace could be operated at a high resistor temperature, with resultant rapid melting of the metal, was in its favor, but the necessity of forcing all of the useful heat through the refractory crucible wall made an efficient heat transfer impossible and high

radiation losses from the outer walls unavoidable. In fact, any direct obstacle to the passage of heat from its source to the material under treatment is an initial handicap very difficult for an electric furnace to overcome, and a refractory barrier is about the worst possible obstacle. The cost of electric heat per unit is high, and a respectable thermal efficiency is a *sine qua non* for successful electric furnace operation in all cases where the electric method enters into competition with combustion furnaces.

At least two independent attempts were made to improve the thermal efficiency of the crucible furnace by building it in multiple-crucible form, with resistor elements suitably arranged between crucibles, so that the resistors radiated useful heat from both sides instead of only one. These efforts resulted in a somewhat improved thermal efficiency but the practical objections to this type of construction were such as to prevent its further development.

There are on record several patents which propose that the crucible shall be heated by arcs suitably disposed around its circumference. In one case it is even suggested that arcs be maintained between several surrounding electrodes and the walls of the crucible itself! So far as known, none of these designs was ever actually tried out. The use of an arc in this manner would not greatly improve the thermal efficiency as compared with the use of a high-temperature resistor, while the crucibles would certainly be subjected to very severe punishment.

Darwin tells us that a species which has apparently become very well stabilized and has failed, for a considerable time, to produce any new varieties, will occasionally surprise one by giving birth to new and startlingly different offspring. The electric furnace is no exception to this rule. The latest proposal to melt brass in an electric crucible is one which has recently been very thoroughly described and discussed, in which the metal within the crucible is heated by a high-tension, high-frequency induction or eddy current. The walls of the crucible itself are electrically conducting and serve to heat its contents during the period while the metal is still solid and in pieces not in good electrical contact with each other. The heat does not have to be forced through the refractory wall of the crucible and there is no reason why the thermal efficiency should not be high. The refractories are not

exposed to an intense heat source and should be very long lived. There are no carbon parts to burn away and be replaced.

Most of the disadvantages already described as characteristic of the crucible furnace have been overcome in this design. This new type has, however, so far been built in sizes more suitable for the laboratory than the foundry, and there are obvious electrical difficulties in the way of its construction for a capacity of more than, say, 200 pounds of brass. At least it is not yet in commercial use for brass melting and its future development is a subject for speculation rather than prophecy. In the small-scale production of carbon-free metals and alloys it has already filled a need not previously satisfied by any type of melting equipment.

As a matter of fact, any electric crucible furnace necessarily falls short of the standards now set for electric brass melting. The capacity of any single unit is small and it is cumbersome when compared with combustion furnaces of similar capacity. One of the principal secondary advantages of the electric furnace is the large production possible from a single unit, reducing the amount of attendance and floor space necessary. Furthermore, crucibles are so expensive and so short lived that their elimination from the foundry is, in itself, a saving of no small magnitude to be credited to electric melting.

The low thermal efficiency of crucible furnaces heated from without naturally suggested the possibility of utilizing the walls of the crucible itself as a resistor. This principle was tried out quite thoroughly rather early in the development of electric furnaces for melting brass. In one type the crucible was built of a special mixture with suitable electrical conductivity but no attempt was made to insulate the walls of the crucible from the metal which it contained. Naturally enough, most of the current took the shortest and easiest path and passed through the metal rather than through the surrounding walls, with the result that the heat generated was entirely insufficient for the purpose.

In another design this feature was taken care of by means of a special insulating lining separating the conducting walls from the metal. It proved almost impossible, however, to maintain this insulating layer, and short circuits invariably resulted. Another serious difficulty lay in the fact that the temperature in the interior of the conducting wall frequently became so high as to cause a

chemical reaction between the carbon and the earthy material in its composition. This reaction destroyed the crucible and made necessary its replacement at frequent intervals. This type of furnace was supposed, at one time, to be in very successful commercial use in Germany, but it failed entirely in this country. At present there seems to be no real evidence that electric brass melting has ever been on a commercial basis in Germany, either with this or any other type of furnace.

Not all, even of the early experimenters, limited their attention to the crucible furnace. The advantages of a larger furnace capacity and the elimination of crucibles were sufficiently obvious, and had already resulted in a considerable use of various types of direct-flame oil and gas furnaces. The earliest attempts to melt brass electrically in a furnace of this sort made use of an incandescent resistor supported above the bath and radiating heat directly to the metal. This construction, applied to an open-hearth furnace of small capacity, gave rapid melting and a fairly high thermal efficiency. The principal difficulties were two: the development of a resistor which would stand up continuously under the required conditions without an excessive maintenance cost, and the invention of some reliable method for supporting the resistor in the desired position over the bath. Neither of these basic problems has ever been adequately solved.

Overhead resistors of carborundum, carbon, graphite, and molded carbonaceous mixtures have been tried without success. The carbon blade resistor was moderately successful in a small furnace of this type, but its high maintenance cost continued to be a handicap. In furnaces with a metal-holding capacity much exceeding 300 pounds the mechanical problem of supporting this or any other type of overhead resistor has never found a practical solution. A refractory ceiling over the bath, supporting the resistor and separating it from the bath has been tried but interferes too seriously with the attainment of a high thermal efficiency. Various means have been suggested for coating the resistor with a protective coating which would prevent oxidation and thus prolong the life of the resistor material. None of these has proved practical, although a new furnace of this type now being developed is said to have an "indestructible resistor." If this proves true, a difficult problem of long standing has been solved.

The difficulties which interfere with the use of an overhead resistor are partially avoided if the resistor is located above the bath, but at either side or surrounding the central portion of the melting chamber. In this way the resistor can be supported at all points by the wall of the furnace itself. In this type of construction little heat reaches the metal by direct radiation, most of it radiating to the roof and walls of the furnace and thence to the metal. This method of transmitting heat is not conducive to high efficiency but is less objectionable than the necessity of forcing the heat through a crucible wall or other refractory barrier.

One well-known type of furnace now in commercial use employs this principle, utilizing for the purpose a granular resistor contained in a nearly circular refractory trough. This trough is exposed to very severe usage since the resistor temperature must be much above that of the molten metal. The roof also is at a temperature considerably in excess of that of the metal and must be highly refractory. In order to prolong the life of the trough and the roof to a reasonable degree, it is necessary to limit the rate of power input to a relatively low value, thus reducing the melting speed and lowering the thermal efficiency. In any case, a high thermal efficiency can hardly be expected in this design, since the heat must travel a long path from its source to the metal and the entire inner structure of the furnace is at a temperature considerably higher than that of the metal.

Another type of furnace which is in somewhat limited commercial use employs a combination of granular resistor and smothered arcs at either end of the melting chamber. In this type also most of the heat must first be radiated to the roof and then to the metal. The characteristic of this furnace, as to melting speed and efficiency, are very similar to those of the furnace last described. The principal difference is that an attempt to increase the rate of power input has, instead, increased the trouble experienced with failure of the refractories.

A high thermal efficiency was early recognized by several of the more far-seeing investigators in this field as an absolutely essential qualification for the permanently successful electric brass melting furnace. It seemed obvious that if some practical method could be devised for generating heat in the metal itself, conditions most favorable for a high efficiency would be produced. This

was already being done with some success in the induction furnace for melting steel, but the high electrical conductivity of copper and its alloys complicated the problem.

The justly celebrated pinch-effect phenomenon is too well known and has been too often discussed to require definition here. Suffice it to say that the pinch-effect can be utilized to increase substantially the electrical resistance of molten brass through which a heavy electric current is flowing. This was done with considerable success in designing the first practical direct-resistance furnace for brass. Molten brass, in channels of small cross-section, was heated by the passage of a heavy current at a low voltage, and, by action of the pinch-effect was forced from these channels into the main melting chamber above, where it gave up its excess heat to the colder metal in this chamber. This process continued indefinitely under conditions which were not only favorable to rapid melting at a high efficiency but also caused a vigorous stirring of the molten metal, a feature which was found to be highly beneficial, for reasons which will be more fully considered a little later.

However, despite the fact that no part of the furnace was exposed to any temperature greater than that of the metal in the resistor channels, and the radiation losses from the furnace structure were consequently very low, the net efficiency of this furnace was by no means high. The heavy currents and low voltages employed necessitated the use of massive copper electrodes which had to be extensively water cooled. The heat lost in this cooling water and by radiation from the electrodes was so great as to reduce the efficiency to an undesirably low value.

It has recently been proposed to change the construction of this furnace in such a way as to eliminate the massive metallic electrodes. The electrodes are to be made up of multiple rods or bands, permanently built into the furnace walls, making contact with the metal in two neighboring hearths which are separated by a refractory wall. These hearths are connected through the wall by one or more channels in which heating is to take place and the heated metal to be expelled by pinch action. In this way the electrodes are removed from the immediate vicinity of the heat source, a change which, in conjunction with the modified design of the electrodes themselves, is calculated to improve the

efficiency of the furnace. No operating data on the performance of this modified design are as yet available.

The elimination of electrodes from the design of the direct-resistance furnace was evidently of the highest importance. This was done in a somewhat later type of furnace by constructing it as a vertical-ring induction furnace with the resistor channels joined at the bottom to form a complete circuit for the passage of electric current. Other conditions remained as favorable as before and an excellent thermal efficiency was now obtained. The vigorous stirring of the metal induced by the pinch effect continued to be a valuable characteristic of the furnace. Within its limitations, this type of furnace is in highly successful commercial use.

The limitations of the vertical-ring induction furnace are due, first of all, to the fact that it is an induction furnace and, as such, cannot be constructed in large sizes without introducing electrical disadvantages such as low power factor. In sizes up to a capacity of about 600 pounds of brass this difficulty is not encountered to a serious degree; in larger sizes—which for this reason are not attempted—the furnace cannot be operated satisfactorily at commercial frequencies. Since the furnace must be started with an initial charge of molten metal, and cannot be allowed to cool down more often than once a week without serious injury to the refractory resistor channels, it must either be operated 24 hours per day or at least operated over night at a power input sufficient to hold molten a small charge of metal.

The furnace cannot readily be changed from one alloy to another, since its electrical characteristics depend upon the electrical resistance of the alloy in use, for which the dimensions of the resistor channels must be specially designed. Furthermore, a change of alloy makes necessary draining the furnace completely and starting with a new charge of molten metal melted in some other furnace. As a result of these limitations, the furnace is not recommended by its sponsors for more than one class of commercial service, 24 hour operation melting yellow brass. The relatively high electrical conductivity of the high copper alloys are a source of difficulty in any type of direct-resistance furnace.

The widespread success of arc furnaces in the melting of steel was not overlooked by those more particularly interested in the brass industry. Many attempts were made to apply both direct

and indirect arc furnaces directly to the melting of brass, without changing the design which had been found most suitable for steel melting. These attempts were pretty uniformly unsuccessful, for the reason that copper and its alloys—particularly the high-zinc alloys—suffered under the direct application of such a high temperature heat source as the electric arc. Metal loss, both by oxidation and volatilization, was decidedly excessive in these furnaces, and the principal advantage of electric melting as compared with melting in fuel-fired furnaces was lost when no metal saving could be shown. In fact, in many instances, metal losses were heavier in electric arc furnaces than in combustion furnaces in common use. At the same time it was learned that the arc type of furnace had many advantages as compared with other types of electric furnaces which had been proposed and tried out. Simplicity of electrical design, rapid and efficient melting, and low maintenance costs were all in favor of the arc method.

A great deal of time and study was devoted to the discovery of some method which would make possible the utilization of the good features of the electric arc for brass melting without experiencing the objectionable ones. The direct type of arc furnace was evidently out of the question since there was no way of avoiding local overheating of that portion of the bath which was so unfortunate as to come into direct contact with the arc. In the indirect arc furnace, overheating was less localized and was experienced to some extent throughout the entire surface of the bath which received direct radiation of heat from the arc. It seemed probable that if the metal could be stirred with sufficient vigor, the entire bath could be maintained at a uniform temperature and tendency toward local overheating could be entirely neutralized. It was found by experiment that rocking the furnace mechanically, at the rate of approximately two oscillations per minute, resulted in a degree of agitation ample to maintain complete uniformity of temperature throughout the molten bath, and that the obvious advantages of the arc furnace could be utilized in this way without the slightest injury to the metal, even in the case of alloys containing 40 percent or more of zinc.

The so-called rocking electric furnace resulted from this development and is in wide commercial use at the present time for melting all classes of copper alloys, as well as copper itself. This

furnace is cylindrical in form and is oscillated by means of gears actuated by an electric motor. The thermal efficiency of the furnace is on a par with that of the vertical-ring induction furnace and higher than that of ordinary types of arc furnaces, largely because such of the refractories as are exposed to direct radiation from the arc give up their excess heat to the molten metal which washes over their surfaces. This regenerative cooling of the brick-work also prolongs the life of the refractories appreciably. As in the induction furnace, the vigorous stirring of the metal results in a uniformity of temperature unattainable in any stationary type of melting furnace. It also results in remarkable uniformity of composition throughout the alloy, a feature which is of particular importance in the melting of high-lead alloys.

The pronounced success of the rocking type of arc furnace has prompted many suggestions for modified designs, similar to it in principle but differing from it in details of construction. For example, it has been proposed to rotate the furnace body instead of merely oscillating it. This and other modifications have not yet received a thorough test in commercial use. It may be said, however, that the constant tendency of real progress in furnace design is toward simplification, and that changes which oppose this tendency are not likely to meet with marked success. Complication of design can only be justified on the ground of greatly increased simplicity of operation. Even then the mechanism must remain as nearly fool-proof as is humanly possible, and must not require any great amount of skilled attendance to keep it in good working order.

The evolution of the electric brass furnace has now proceeded to such a point that fundamental improvements in design are henceforth likely to be rather slow to materialize. There will, of course, be constant progress in the development of refinements in mechanical and electrical design, calculated to make the furnaces more reliable, more durable, and more nearly fool-proof than they are at present. One of the most fertile fields for such improvement is in the development of refractories more exactly suited to the requirements of electric furnace operation. But in metallurgical design the resistance furnace, the induction furnace, and the arc furnace are likely to remain pretty much what they now are for some time to come.

This brings us to a brief consideration of what the brass foundryman at the present time can expect and ought to realize from the use of electric furnaces.

The first and probably the most important point is the saving of metal—commonly wasted during the melting process—which electric melting makes possible. If the charge to be melted consists of new metal or clean scrap, the net metallic loss during melting and pouring from the furnace should not exceed one percent for yellow brass and 0.5 percent with red brass. With clean yellow brass, containing 40 percent of zinc, losses as low as 0.75 to 0.85 percent have been experienced as an average for a considerable tonnage of metal melted. In melting a scrap charge containing a high percentage of non-metallic, such as oily borings, chips, grindings, etc., the net loss should not exceed two percent. Very low losses are possible in all three of the furnace types mentioned as being in widespread commercial use. Such advantage as there is lies with the induction and rocking arc furnaces, since in these the metal is stirred so vigorously that local overheating of any part of the bath is practically impossible, while in any furnace which melts the metal without stirring it some degree of overheating in that part of the bath most directly exposed to the application of heat cannot be avoided.

It is also true that the furnace which melts without agitation is not particularly well suited for melting a charge which contains a high percentage of finely divided, dirty scrap, while these can be handled without difficulty in either induction or rocking arc furnaces. In the unstirred bath the unmelted portion of chips and dirt tends to float on the molten part of the charge, screening it from the application of heat, and thus seriously reducing the efficiency and causing lack of uniformity in heating. Scrap of this nature must intermittently be submerged in molten metal in order to melt rapidly and uniformly.

Brass melted in the electric furnace is practically free from metallic-oxide drosses and has no opportunity to pick up sulphur or other contamination from combustion gases. Again, however, those furnaces which stir the bath have a considerable advantage in that they produce metal of remarkably uniform and homogeneous composition. This is a particularly important point in the melting of high-lead alloys, which can be melted in the rocking

arc furnace without the use of additional stirring. The same thing holds as to uniformity of temperature of the metal as it is poured from the furnace, which can only be attained by thorough mixing during melting.

The consumption of electric energy under average conditions of 8 to 10-hour operation is as low as 240 kw. hrs. per short ton for yellow brass, and 275 kw. hrs. per ton for red brass, in the induction or arc furnaces. In 24-hour operation figures as low as 200 kw. hrs. per ton or less, have been obtained. Less efficient furnace types use from 400 to 500 kw. hrs. per ton, depending upon conditions.

Flexibility, which in this case may be defined as the suitability of a furnace for radical changes in operating conditions or for an abrupt change in the composition of the alloy to be melted, is a marked characteristic of the resistance and rocking arc furnaces which is notably lacking in the induction furnace. This factor is one of great importance in the foundry or smelting plant. As already stated, the induction furnace is practically limited to 24-hour operation with a single alloy composition.

The net melting cost, considering all factors which should properly be considered under this head, is naturally lower in those furnace types which melt the metal most rapidly and efficiently, since their use of electric energy is more economical and their higher rate of production reduces the fixed charges per ton of metal melted. In many cases, the cost of electric melting is not more than half the cost of melting the same alloy in combustion furnaces. Even in the less efficient furnace types, electric melting is usually less costly than the older methods. This fact, taken in conjunction with the fact that the electric furnace saves some 75 percent of the metal losses common, in greater or less degree, to all fuel-fired furnaces, should be sufficient to convince the most sceptical that the present rapid growth of electric brass melting is based on a solid economic foundation.

Electric brass melting can no longer properly be called "the coming thing." It has arrived in a most convincing fashion, as is evidenced by its rapid adoption by the larger and more progressive rolling mills, foundries, and manufacturing establishments which use brass in large quantities. The three furnace types which have been most prominently mentioned in this discussion, are sharing

largely—although by no means equally—in this growth. The flexibility, economy, and high quality of metallurgical performance of the rocking arc furnace are factors which combine to make it the most widely used electric furnace in the brass industry.

DISCUSSION.

C. A. WINDER[1]: On page 592 of this paper it is stated that brass can be melted with as low as 240 kw. hours per ton, but when we go to melt it, we do not get the result with 240 kw. hours per ton, it is usually considerably higher. That, of course, does not mean that it cannot be done, it just usually is not done. Now you can put plenty of heat into any type of furnace that has heat capacity, and throw into that furnace some metal after you have put in sufficient heat, and can get out heats that are as low as this figure, perhaps a little lower; in fact, there is no reason why you could not get a heat out of a brass furnace without any input of power if you have sufficient heat capacity and have raised that capacity to the proper temperature prior to charging, but that is not operation. There are a number of other points that I think it would be well to consider. One is that brass melted in the electric furnace is practically free from metallic oxide drosses, and has no opportunity to pick up sulphur and other contamination from combustion gases. That is too little appreciated. If any of you have ever had experience in reverberatory furnaces in the copper industry, you will realize what it means to pick up sulphur in molten copper, and that it is a very expensive process to start out with a chemically pure charge and end up with one seriously contaminated. In the electric furnace that is a matter that is controllable, and inasmuch as you are putting into the furnace pure heat, there is no reason for contamination from that standpoint. On the other hand, it is not entirely free from oxides, and there is the point in which the arc differs radically from the resistance furnace and still more from the induction furnace. The resistance furnace is not so apt, if properly designed and having a small amount of area or volume above the bath to hold oxygen, and is not as apt, owing to the lower temperature

[1] Southwest General Electric Co., Phoenix, Ariz.

of its heat source, to oxidize the zinc. On the other hand, the induction furnace has the added advantage that in an electric circuit where the current is passing through the metal itself, there is a squeezing action of the surrounding magnetic field which tends to force out the molten bath in the channel of the induction furnace, anything that is non-conductive; consequently we have a cleansing action going on in the induction furnace, tending to keep the metal free from oxides. An added feature is that the brass furnace of the induction type can have a smaller crucible than the other type, it having the heat generated within the metal itself and does not lose as much heat by radiation from the heat source. You know the question comes up as to the uniformity of the temperature in the metal itself, and the question is brought up that the rocking furnace maintains a more uniform temperature in the metal itself. That of course is a question. The source of heat in the arc furnace of course is the highest known source of heat, and direct radiation over a few inches from a source of heat of that temperature does not lead us to believe that the receiving medium is very much below the temperature of the sending medium of that heat. Now we all know that zinc boils at a very low temperature, and that is one of the things we have got to look out for in any type of arc furnace, the tendency to boil off the zinc, and that is again where the lower temperature furnaces are an improvement over the arc type, and, of course, the induction furnace has it over all of us in that, the metal itself being the source of heat, everything else in the furnace is at a still lower temperature than the metals, and consequently we do not have the same trouble.

As to the universal use of the electric brass furnace, there is hardly any question of a doubt but what at least 50 percent of the present melting capacity of this country can be electrified at a distinct saving. There is a very distinct field for each and every brass furnace that is on the market at this time, regardless of the survival of the fittest. There is no question but what there is a place for the arc furnace, whether it rocks, rotates or gyrates. It is perfectly simple, there is a place for it as there is a place for the resistor type, and there are just about as many resistor types of furnace on the market as there are arc furnaces, and there is

distinctly a place for the induction furnace, of which there are two or three times as many as all the rest put together; so at the present time there is no complete segregation of the arc furnace from all the others, and other types are still possible and have not been relegated to the scrap heap.

E. L. CROSBY[2]: The only evidence we can offer to combat the suggestion that brass may be but is not being melted for 240 kw. hours per ton is that today we would be delighted to take you, individually or collectively, to any one of eight or ten installations of Detroit furnaces which are every day in regular production, melting brass of sixty-forty, or as high as seventy percent copper content for 240 kw. hours, or less, per ton average input. That does not mean for one heat; that does not mean a test heat; that does not mean a third or a fourth heat, after the furnace has become hot; that means every heat during the day. We have had users of Detroit furnaces who have had their furnaces in operation for six months, who have reported to us from their regular operating cost data sheets, that their daily tonnage usage of energy on 60-40 brass is as low as 215 kw. hours per ton, not 250 kw. If we had a furnace operating eight hours per day, not twelve, not eighteen nor twenty-four, but in regular production on 60-40 brass 8 hours per day which required 240 kw. hours per ton, we would know something was wrong either with the furnace or with its operator; we would not expect it to continue on that basis; we have not one that is taking as high as that. It is true that a furnace manufacturing bronzes, 92 percent copper, with other materials requiring a high melting temperature, will not operate for 240 kw. hours per ton, and I do not believe that anyone connected with our organization ever suggested that it would. Regarding the matter of uniformity of temperature throughout the bath—I would like to suggest to Mr. Winder that when he said there would not be a whole lot of difference between the temperature at the source of heat and the temperature of the metal leaving the furnace, that unless there was a whole lot of difference, there would not be much metal left in the furnace, because the temperature of the arc is around 4,000° C., while the pouring temperature of the metals is around 1,200° or 1,300° C., and I do not believe any copper-zinc alloy would stand raising to the arc tem-

[2] Vice-President and General Manager, Detroit Electric Furnace Co., Detroit, Mich.

perature. The uniformity of temperature best demonstrated by tests taken at various parts of the bath immediately on the cessation of the rocking, shows a variation in temperature of not over 3 degrees throughout the entire charge, and that is simply within the range of pyrometer accuracy in the average foundry. It means that the temperature is uniform, and it seems obvious that if you have a charge of 2,000 pounds of metal which is being rocked, and there is a movement in two directions through that bath at the rate of a complete cycle of rocking every 40 seconds, it is impossible to believe there will be any marked difference of temperature throughout that charge. Furthermore, I cannot conceive how it is possible to have any particularly distressing difficulties with oxides in an atmosphere which, from within 10 minutes from the time the arc is put on (which means long before any metal becomes molten) possesses a very distinctly reducing atmosphere. There being no oxide introduced in the furnace by any other method, I cannot conceive of your having any particular difficulty with oxides in your resultant metal, and furthermore, the results obtained in actual practice show no difficulty from this source.

The paper which Mr. St. John has presented is not the result of theory, it is the result of actual use of our furnace in the brass-melting field, in the foundries, rolling mills, smelting and refining plants; and while we are not blessed with installations to so great a number as some of our friends, we have about fifty furnaces in actual operation, I believe that in the actual tonnage melted per day, we compare very favorably; as a matter of fact, I think it is probably something over twice that of any other single manufacturer who has perhaps presented figures which do not exactly agree with those we are giving.

S. A. TUCKER[3]: I would like to inquire what influence the advent of the electric furnace in this branch of metallurgy has had on the use of crucibles? We have had a great deal of discussion as to crucible manufacture at one period of the war, because imported graphite and clay were entirely shut out, and I hinted at that time that the electric furnace was probably going to settle the business. It does look as though it had a marked influence at the present time.

[3] The Chemical Foundation, Inc., New York City.

H. W. GILLETT[4]: As to melting brass, operating 24 hours a day, the American Brass Company says that with every condition right they can hit 174 kw. hours per ton; but the Bridgeport Brass Company on a smaller size furnace, had a shop average of some 225 kw. hours per ton. Brass and bronze are two different things. If you take regular yellow brass, any real honest-to-God furnace ought to melt it, on 24-hour operation, at under 240 kw. hours per ton, with all the delays in shop practice, with shop practice anywhere near decent. As you climb up to higher melting alloys, your power consumption increases. As to rocking and rotating furnaces, it seems to be more or less a question of fact. Until we get the facts, there is not an awful lot to be said. In a rocking furnace, unfortunately, the force of gravity is always present; the metal, after it gets partly melted, is more or less sticky. If you rock all the way around and carry up a heavy ingot to the top of the furnace, it is very likely to fall, and sometimes falls on the electrodes, and if it does, the Acheson Graphite Company pays more dividends. I remember in an experimental test I broke 4 electrodes inside of 20 minutes, breaking one pair and putting in another, and then breaking them. With a rocking furnace, you have to be careful not to rock too far, too soon, otherwise you will break the electrodes. I am open to conviction, but I do not see how you can stir your metal satisfactorily and avoid local superheating without getting the furnace in motion before you have got your melt all down, and I don't see how you are going to rock before that without smashing electrodes right and left—that is, a man-sized furnace; on a toy furnace like we had in the laboratory at Ithaca, I do not think we ever broke an electrode; it was so small, using small ingots and small charges, we did not break any electrodes and did not have any trouble, and it is very possible that a rotating furnace in the smaller sizes may work well, but I look forward with great interest to the trial of a rotating furnace in the 1-ton size on yellow brass; that will give us some information. Mechanical charging can be readily done in a furnace with the door on the circumference, and far less readily with a door on the end. Refractory life would be longer if you could rotate completely, but the complete rotation involves the proposition of carrying currents around 2,000 or more amperes

[4] U. S. Bureau of Mines, Ithaca, N. Y.

on a man-sized furnace; and a sliding contact of any sort is rather difficult to maintain in a foundry, with the smoke and dust and dirt that is there. We considered rocking and rotation and various other things, and came to the conclusion that in the first trial development of the idea of stirring the metal by moving the furnace, it would be just as well if we had the leads solidly connected to the electrodes. If Messrs. Booth and Ryan are successful in their development, I will be the last to fail to give them credit for it, and I think, as Mr. St. John has pointed out, that everything is an evolution. If the change from rocking to rotation is an improvement, the people who are sponsoring that will certainly be given credit.

CARL HERING[5]: One of the difficulties in brass melting is to keep the zinc from volatilizing, which means a loss of zinc, and a change of composition. The reason is that the boiling point of zinc is lower than the casting point of brass.

J. W. RICHARDS: That is true only of pure zinc, not of the zinc in brass.

CARL HERING: Zinc will not boil out of brass at quite that low temperature, but it does tend to boil out at casting temperatures and it is important to prevent this loss of zinc, not only because it is a loss of metal, but also because it changes the proportion of the zinc and copper in the brass. It may therefore be of interest to call attention to the fact that in a certain type of electric resistance furnace which has been referred to and in which the brass is heated by the passage of the current through the metal itself enclosed in a kind of tube, there is a self-regulating feature which is quite important: the hottest metal is that in the resistor itself, and when that temperature reaches the point at which the zinc boils out of the brass the vapor forms a bubble and this breaks the circuit, so that on the ammeter one can tell at once whether the point has been reached at which the zinc is boiling out of the brass. There are at present, I understand, 84 of these furnaces in use, chiefly in the wrought brass industry; the operators are instructed to watch the ammeters and if they kick, then the current must be cut down as the temperature is then getting too high. This self-regulating feature prevents the loss of zinc in that type of furnace.

[5] Consulting Electrical Engineer, Philadelphia, Pa.

E. F. CONE[6]: Mr. Winder spoke of the future of the use of the electric furnace in melting non-ferrous metals, particularly brass, and the extent to which it had already been introduced. I can give a few figures of interest. On the first of March there were between 260 and 265 furnaces of all types melting non-ferrous metals in the United States, and since then there have been enough added to bring the total up to 300. Most of that development has been in the last two years. Contrasted with the steel industry, which has been of course a marvel of development, in seven years there have been only 323 units, or something like that, installed in the United States steel industry.

H. W. GILLETT: There are seven large brass furnaces in actual operation that have not yet gotten into any of those lists at all.

F. S. WEISER[7]: There seems to be quite a difference of opinion in regard to the merits of the various furnaces and their power consumption. But there are also other important features in electric furnaces, and in order to shorten this argument, I think the exponents of the various furnaces ought to tell us something about the total and the net metal losses and how they arrive at them. Also the lining life, and time necessary for relining.

T. F. BAILY[8]: I feel a little embarrassed about getting up here when we have to confess right away to 285 kw. hours per ton in our furnaces even in the best practice, but we do find that there are more important factors than the current consumption; in fact, that is a secondary consideration. I should say that the first consideration in designing a brass melting furnace would be to bear in mind that the fellow who will operate it will operate it with a sledge and a crowbar, because those are about the only tools he has around the place. The foundry operations, such as holding the heats and making them fit up with the foundry floors is another very important feature. I should say that most of the furnaces that we have in operation on yellow brass are taking, even on 10-hour operation, about 400 kw. hours per ton, they will probably average 500 kw. hours per ton, which, according to some other makers, in fact two makers, is more than twice the average consumption of their furnaces, and yet we seem to be

[6] Associate Editor, *The Iron Age*, New York City.
[7] Asst. to Supt., Elec. Trans. Dept., Scovill Mfg. Co., Waterbury, Conn.
[8] General Manager, Baily Electric Furnace Co., Alliance, Ohio.

able, either by salesmanship or some other way, to get a fair percentage of furnaces, especially the others that are coming out. I think we have in actual operation about 50 furnaces and probably 25 more that are going in. About five of those will probably be for aluminum, and the rest yellow brass or bronze, possibly, yellow brass foundries. As to lining life and upkeep, that is another very serious consideration. The fellow running a furnace, if he has trouble with it, will throw it out no matter what his economies are; it is a case, more particularly in average practice, of having a melting unit that will melt whenever you want it to melt, even if its average cost is much higher than some of the typical makers. For instance, take the Ajax furnace, I believe there are very few in foundry practice, and yet I think they have substantially all the rolling mill business; they make most excellent brass, as good a brass as is made in any furnace without any question, but they are not particularly well adapted to foundry practice, due to the fact that perhaps they require cleaner metal to operate with, and also the mechanical features about the furnace, such as the size of the charging door, convenience of operation, being able to shut the furnace down at any particular time without injury. As I understand it, the induction furnace has to be kept hot 24 hours a day, while a furnace that has an open hearth, whether an arc or resistor, can be shut down at any time. Another factor lost sight of is the matter of renewals and repairs; for instance, in competition with other manufacturers, we usually mention electrode costs as compared with electrode type furnaces, and somewhat higher renewal and upkeep cost in the induction furnaces in keeping the tubes up, and the cost of repairs in case of an accidental power shortage which may freeze up the furnace, so that really this matter of current consumption which used to scare us so badly in years gone by does not seem to be much of a factor, so far as the mere furnace builder and operator is concerned. I think that is all I have got in mind here, unless some one has got a question with which they would like to drag something else out of me. I might mention metal losses. It has been our experience on yellow brass scrap, on anything excepting borings, that the metal losses will run about 1 percent, and on new metals, the losses in say 60-40 or 65-35 grades seldom run above ¾ percent in regular shop operation.

C. A. WINDER: There is one other feature that is usually conceded to be of importance in making brass, and one thing which has not been mentioned, and that is in such brasses as contain an appreciable percentage of lead. Up to the present time the induction furnace, on account of the character of its lining, has not been able to utilize that method of heating on those brasses having over 2 percent lead, on account of the fact that the lead attacks the lining and chokes up the channel. On the other hand, the reverberatory type of furnace, the arc resistance and resistor type and the arc type are able to handle that class of work and the statement is made that the rocking or rotating will mix the metal, so that the lead is always uniform. In talking with one of the brass makers recently who has experience with lead mixtures, he brought up the point that he felt that the resistor type of furnace, or rather the reverberatory type, using a broad, shallow bath, was probably preferable to a small, narrow and deep bath in that the lead never formed an alloy in the brass, but was always a mechanical mixture, and that while melting there was no difficulty in the rocking of the deeper bath type of furnace. When the rotating or rocking was stopped and the charge poured into the castings there was a possibility, which he found a great probability, of the settling out of the lead during the pouring process. He felt, although his experience did not cover the point, that with the shallower type of bath it was less probable that this would be so marked in the same length of time. Furthermore, he expressed the desire that in any furnace that operated on that class of work there should be some means of access to the bath whereby stirring might be carried on during the pouring.

To correct an impression I apparently left, I do not want you to think that my statement regarding the low kw. hours per ton referred to the induction furnace at all. I appreciate that that is being done regularly at a very much lower figure than 240, and probably will be for a long time to come. As to the life of linings, recent investigations showed that in the induction furnace we are getting as high as 3,000 heats out of linings, which is a marked improvement over the old ones, and apparently the process of improvement is still going on, so that we may hope that the cost of linings in the induction furnace will improve from time to time.

On the other hand, the higher rates, as Mr. Baily has so aptly pointed out, of power consumption in the other types of furnaces, such as the arc resistor, furnaces of the arc type and the resistor type, as Mr. Bailey so well knows, have not met with any serious objections, and those furnaces fit well in foundry practice, where ease of pouring and handling is of prime importance and no inventive genius is necessary to handle the metal after it is melted.

H. W. GILLETT: As a matter of justice to the induction furnace, those figures on lead should not be allowed to stand. The makers, who have been most commendably conservative, have never advocated over 3 percent lead. Several of the users had very good results and very good lining life with 3½ percent of lead. Mr. Clamer wrote me last week that they had very satisfactory results with 6 percent of lead and they are now experimenting with other types of refractories with the avowed intention of carrying the lead content as high as you want for metal alloys. All these furnaces are improving and everybody begins to realize the weak points in any particular design. All this discussion is bringing out what Mr. St. John brought out and what Mr. Winder said at the start, that there is a field for every one of these types. I do not say that there is a field for every modification of every type, but there is a field for the induction furnace that no other furnace can fill; there is a field for the reverberatory, reflected heat furnace that these others can not very well compete with, and there is a field for rocking or rotating furnaces, and the quicker we can get the impression into prospective users that there are different types of furnaces for different conditions, the better. There is no best brass furnace but there is a best brass furnace, usually an electric furnace, for a given set of conditions. There is no general patent medicine cure-all for every set of conditions, and the present development of the different types is proving that more and more thoroughly every day. Special conditions, sometimes mechanical, sometimes psychological, make one type superior to the other. Take a place where power is cheap, and Mr. Baily's contentions that power costs are entirely secondary, are perfectly true, but only where it is very cheap. Given conditions where you can utilize an induction furnace on 24-hour operation, or any other of the more efficient furnaces, and it is foolish to run a 400 kw. hr. per ton furnace when you can do the same thing at 200.

E. L. CROSBY: Regarding high lead alloys, the Michigan Smelting and Refining Company has melted thousands of tons of material containing 26 percent lead in Detroit furnaces with an average deviation from the charge poured from a 2,000-lb. furnace into ingot of a quarter of one percent lead content, the maximum deviation in any ingot being 6 percent from desired analysis.

J. W. RICHARDS: While I appreciate that the theoretical amount of power required just to melt is not what the brass foundry is concerned with, because it frequently has refining to do and has to hold the metal and superheat it, yet it is interesting to know that per short ton of metal there is required theoretically 130 to 150 kw. hours to melt it. If 200 kw. hours is used, there is an actual net efficiency of 65 to 75 percent; the other 35 to 25 percent supplies all the thermal losses and allows for holding the charge in the furnace. While zinc boils at a low temperature by itself, yet we must not forget that it is only a fraction of the composition of the brass, 30 to 40 percent, and therefore it boils from brass at a much higher temperature than pure zinc boils.

Regarding overheating by an arc the receiving surface of the metal cannot get anywhere near the temperature of the source if heated by an arc; it can be figured out theoretically that the thermal conductivity of the bath is so great that the surface cannot become anywhere very much overheated by radiation from the arc. I thoroughly agree with Mr. Baily that the amount of power required in melting brass is so small that it is one of the minor considerations. The fact, for instance, that one furnace will make brass with a saving of one percent of zinc over another furnace, would mean the equivalent of about 140 kw. hours per ton (at 1 cent per kw. hour), so that a relative saving of two percent of zinc would allow for the power which is ordinarily required for running the whole operation. These other advantages of the saving of metal and of adaptability and ease of working and permanency, etc., are much the more important factors in running a brass furnace.

H. M. ST. JOHN (*Communicated*): I believe that Mr. Crosby has thoroughly covered the question of power consumption as raised by Mr. Winder. Suffice it to say that a consumption of electric energy substantially less than 240 kw. hours per ton when

yellow brass is being melted on a 24-hour day basis is a commonplace in the electric brass-melting industry where either induction or arc furnaces are used. In 8- to 10-hour operation an average overall figure as low as 240 kw. hours per ton has been achieved in more than one plant.

I cannot at all agree with Mr. Winder that the arc furnace is at a disadvantage as compared with the resistance furnace or the induction furnace when one considers the degree to which the metal may be oxidized in these types. Oxidation of the metal requires the presence of oxygen in the furnace. This can be excluded from the arc furnace as readily as from any other type. In any furnace the surface of the metal becomes sufficiently heated to consume any oxygen which may be present in the furnace. As soon as this oxygen is consumed oxidation stops. The temperature of the heat source, or the rate at which the metal is being heated makes absolutely no difference so long as the furnace is tightly closed against the admission of oxygen. As a matter of fact, the induction furnace is at some disadvantage as compared with either the arc furnace or the resistance furnace, for the reason that it contains no highly heated carbon to consume the oxygen which must therefore react with the metal. The use of a charcoal cover over the metal bath is less effective than the presence in the furnace chamber of white-hot carbon resistor material or incandescent carbon electrode tips. In a rather exhaustive series of experiments the Bureau of Mines' Experiment Station at Pittsburgh has found that the atmosphere in the Detroit furnace during the melting period consists of carbon monoxide and nitrogen almost to the exclusion of carbon dioxide and oxygen.

Furthermore, the above statements do not include a consideration of the fact that the metal in the rocking arc furnace is thoroughly mixed at all times after melting begins, and that the bath throughout has a remarkably uniform temperature. Oxidation and volatilization both depend on the actual temperature of the metal surface. Obviously, it makes no difference how rapidly the metal is heated so long as the surface of the metal does not become heated above a critical temperature where volatilization of the volatile constituents is rapid at whatever vapor pressure may exist at the moment. The very low loss of metal actually experienced in the rocking arc furnace and the almost perfect uniformity

of mixture when alloys containing as much as thirty percent of lead are being melted, merely demonstrate that practice and theory are in accord.

I did not intend, of course, to give Mr. Winder the impression that the arc furnace is the only electric furnace which can possibly be used in melting brass, or that it had eliminated all other types from the foundry. Such a contention would be folly. The fact remains, however, that the arc furnace is actually melting a larger daily tonnage than all other electric furnace types combined. It does not exceed all others in the number of furnaces in use, but due to the greater average size of units and its higher melting speed, it does exceed all others in weight of metal actually melted.

I cannot exactly check Professor Richards in the conclusion he draws with reference to the relative importance of metal loss and energy consumption. There is practically no difference in metal loss between the electric furnace types which we have been discussing. The resistance furnace, the rocking arc furnace, and the induction furnace are on a par in this respect. As a matter of fact, no furnace widely used in the melting of brass can show a saving of as much as one-quarter of one percent as compared with any other electric furnace in commercial use for the same purpose.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

HYDROGEN ION CONCENTRATION IN DRY CELLS.[1]

By H. D. Holler[2] and L. M. Ritchie.[3]

Abstract.

Measurements were made of the potential of a manganese dioxide electrode prepared from certain manganese ores, or a chemically prepared manganese dioxide, mixed with fine Acheson graphite. The object was to test these various materials and the relation of their potentials to the concentration of hydrogen ions in the solution in contact with it. It was found that this potential was, in the case of the native ores, a logarithmic function of the hydrogen ion concentration; in the case of the chemically prepared oxide there was no such relation. The cause of this difference is not investigated or discussed. In the case of using the native ores, the logarithmic relation referred to serves partly to explain variations in the open-circuit voltage and polarization with time. [J. W. R.]

I. INTRODUCTION.

In connection with the testing at the Bureau of Standards of materials to be used in the manufacture of dry cells, it became necessary to measure the potentials of some carbon-manganese dioxide electrodes such as are used in dry cells. It was originally planned to make a thorough study of the oxides of manganese in their rôle as depolarizers, with particular attention to the shelf-life of the cell, but since it was necessary to discontinue the work for a time, it was felt that the results thus far obtained might be suggestive to other workers in this field.

[1] Published by permission of the Director of the Bureau of Standards. Manuscript received January 26, 1920.

[2] Chemist, Parlin, N. J.

[3] Bureau of Standards, Washington, D. C.

Several important papers have been published on the manganese dioxide electrode. Tower[4] and Smith[5] studied the electrolytically prepared oxide as a means for measuring the hydrogen ion concentration of organic acid salts. Thompson and Crocker[6] noted the effect of alkalies and acids upon the potential of electrodes prepared from a mixture of granulated carbon and pyrolusite.

Allmand[7] states that the reaction of manganese dioxide as a depolarizer may be represented by an equation such as

$$MnO_2 + \tfrac{1}{2}H_2O \rightarrow \tfrac{1}{2}Mn_2O_3 + OH^- + (+).$$

According to Nernst's equation the electrode potential at 25° would then be

$$E = \text{constant} + 0.059 \log \frac{[MnO_2]}{[Mn_2O_3]^{\frac{1}{2}}\,[OH^-]}$$

$$= \text{constant} - 0.059 \log [OH^-] = \text{constant} + 0.059 \log [H^+];$$

that is, the potential is a logarithmic function of the hydrogen ion concentration.

No experimental data have been published to show whether this relation is true. While the authors previously mentioned recognized that a logarithmic relation exists, and suggested equations representing it, they did not establish their conclusions by measurements with a hydrogen electrode. Moreover, no one has pointed out the significance of the hydrogen ion concentration as explanatory of variations in the open-circuit voltage of dry cells, and the part it plays in the polarization of a dry cell during discharge.

It is therefore the purpose of this paper to present experimental data showing (1) that the potential of a manganese dioxide electrode prepared from certain ores is a logarithmic function of the hydrogen ion concentration of the solution in contact with it; (2) that chemically prepared manganese dioxide does not show the logarithmic relation; (3) that the relation between the potential of the manganese dioxide electrode and hydrogen ion concentration serves as a partial explanation of variations in the open-circuit voltage and polarization of dry cells.

[4] Tower: Zeit. phys. Chem. (1895), 18, 17; (1900), 32, 566.
[5] Smith: Zeit. phys. Chem. (1896), 21, 93.
[6] Thompson and Crocker: Trans. Am. Electrochem. Soc. (1915), 27, 155.
[7] Allmand: Applied Electrochemistry (1912), 206.

II. EXPERIMENTAL WORK.

(1.) *Method of Measurement:*

The method used for measuring the potential of the carbon-manganese dioxide electrode in different solutions was briefly as follows:

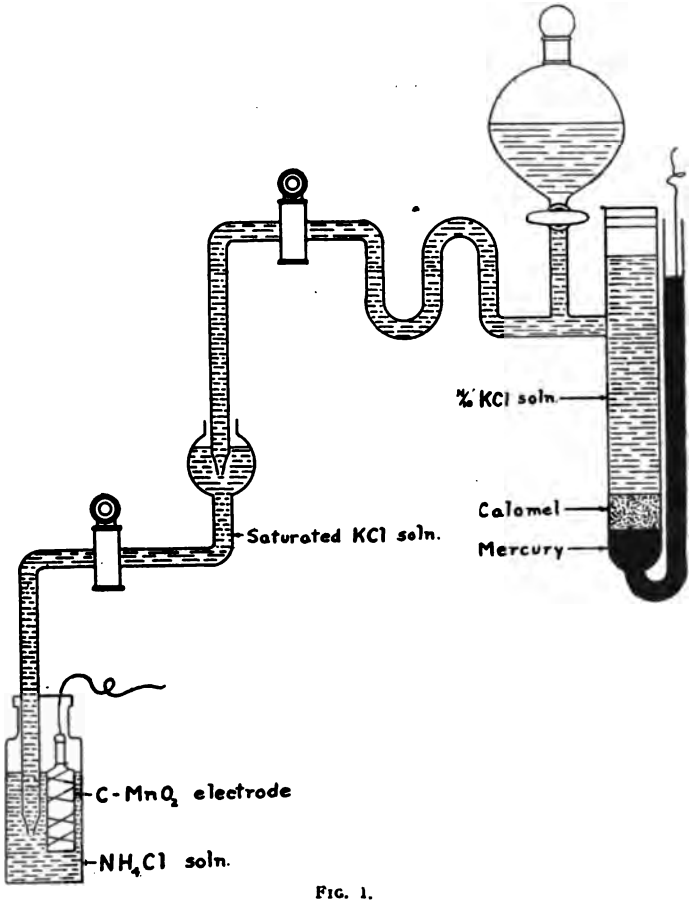

FIG. 1.

The electrode was introduced into a two-ounce bottle containing the solution of known hydrogen ion concentration. Into this solution dipped a siphon containing a saturated solution of potassium chloride, which led to a tenth-normal calomel electrode. This set-up is shown in Fig. 1. The electromotive force of this chain

$$\mathrm{Hg} \,\Big|\, \mathrm{HgCl} \,\Big|\, \frac{\mathrm{N}}{10}\ \mathrm{KCl} \,\Big|\, \begin{matrix}\text{saturated}\\ \mathrm{KCl}\end{matrix} \,\Big|\, \begin{matrix}\mathrm{NH_4Cl\ of}\\ \text{known } [\mathrm{H^+}]\end{matrix} \,\Big|\, \begin{matrix}\mathrm{MnO_2}\\ \mathrm{C}\end{matrix}$$

was then measured with a potentiometer.

(2) *Preparation of Electrodes:*

Because of the variety of manganese ores used at the present time in making dry cells, it was decided to select for this investigation several ores typical of those in use. For this purpose some of the manufacturers furnished[8] a number of ores, of which three were selected for this work.

The materials selected were a Caucasian ore, which is considered to be the best material in all respects for dry cells, a Brazilian ore, which has been used since the importation of the Caucasian ore was interrupted by the war in 1914, a domestic ore, and a chemically prepared oxide. The latter is used in large proportions, mixed with the natural ores for making dry cells of small sizes such as are used in flash-lights.

For use in the electrodes, the ores were ground and sized, the portion between 65- and 80-mesh being used. The chemically prepared oxide was a fine powder, and was not sifted.

The electrodes were prepared from a mixture of two parts by weight of the ore or oxide, and one part of Acheson "D A G" graphite, the fineness of which was such that 99 percent passes through a 200-mesh sieve. This mixture was moistened with water sufficiently to permit molding into small cylinders 33 mm. long and 12 mm. diameter, around a carbon rod 25 mm. long and 5 mm. diameter. The electrodes were then wrapped in filter paper, tied with linen thread and dried at 110° C. The dried electrodes were then ready for use. A copper wire was soldered to a brass cap on the carbon rod, which served as a lead to the potentiometer.

(3) *Preparation of Solutions:*

Solutions of constant and easily reproducible hydrogen ion concentrations were necessary for this work. The simplest method of preparing such solutions is to add to a salt solution of known concentration a definite amount of its acid or base. Fortunately ammonium chloride, which is used in large proportion

[8] Acknowledgment is made of the courtesy of the Burgess Battery Company and the National Carbon Company, who furnished the samples of ores.

in dry cells, is a very satisfactory salt for the purpose desired. The series of solutions used was therefore prepared in the following manner: A solution containing 200 grams c. p. ammonium chloride per kilogram of solution was prepared. To 100 cc. portions of this solution, 1 cc., 5 cc., 10 cc., 50 cc., and 100 cc. of tenth-normal hydrochloric acid or ammonium hydroxide were added. The hydrogen ion concentration of each one of these solutions was determined by the bell type of hydrogen electrode suggested by Hildebrand,[9] and measured against a tenth-normal calomel electrode.

III. DISCUSSION OF RESULTS.

(1) *Hydrogen Ion Concentrations:*

In Fig. 2 Curve V represents the series of ammonium chloride solutions the preparation of which was previously described. The zero ordinate represents the neutral 20 percent ammonium chloride solution. Additions of tenth-normal ammonium hydroxide to a volume of 100 cc. of the salt solution are indicated from zero to the right, and similar additions of tenth-normal hydrochloric acid to 100 cc. of the salt solution are indicated from zero to the left. The range in hydrogen ion concentration thus obtained is 10^{-1} to 10^{-8}. The uncertainty of the potential of the hydrogen electrode in ammoniacal solutions, due to loss of ammonia produced by passage of hydrogen, makes the alkaline part of the curve a little doubtful, but the error is believed to be small.

The alkalinity of the ammonia is considerably reduced by the presence of the ammonium chloride. Thus, in the solution prepared by adding 100 cc. of tenth-normal ammonium hydroxide to 100 cc. of 20 percent ammonium chloride, we really have a twentieth-normal solution of ammonia containing 10 percent of ammonium chloride, and with a hydrogen ion concentration (Curve V) of 10^{-8}. The hydrogen electrode in twentieth-normal ammonia without the salt showed the hydrogen ion concentration to be 10^{-10}. That is, the presence of 10 percent of the salt reduced the hydrogen ion concentration by one hundred fold. Similar calculations were made by Blum,[10] using the ionization constants of ammonia and water.

[9] Jour. Am. Chem. Soc. (1913), **35**, 864.
[10] Blum: Bull. Bur. Stand. (1916), **13**, 521.

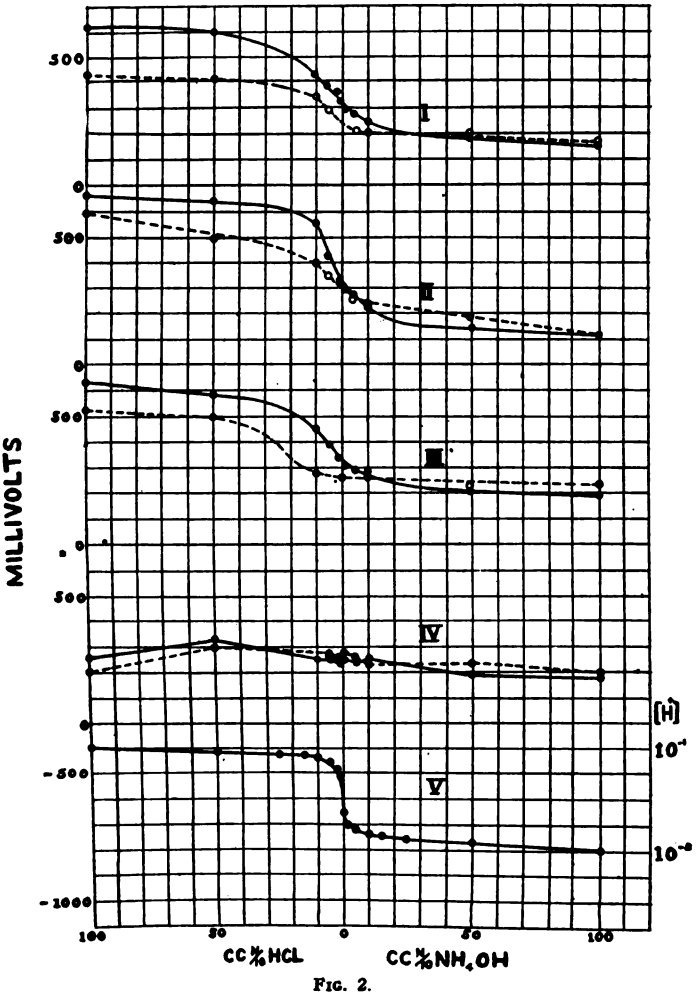

FIG. 2.

(2) *Potential of Manganese Dioxide Electrode:*

The potentials of the three samples of ores and oxide are represented by the curves in Fig. 2; Curve I for the Caucasian ore, Curve II for the domestic ore, Curve III for the Brazilian ore, and Curve IV for the chemically prepared oxide.

In the case of the ores, although the parallelism is not exact, it appears that the potential is a logarithmic function of the

hydrogen ion concentrations. Thus while the potential of the hydrogen electrode in Curve V decreases (— 0.39 to — 0.79)= 0.40 volt, the potential of the Caucasian ore decreases (+ 0.62 to + 0.15)=0.47 volt, the domestic ore (+ 0.67 to + 0.11)=0.56 volt, and the Brazilian ore (+ 0.64 to + 0.19)=0.45 volt. That is, for each ten-fold decrease in hydrogen ion concentration the potential of the Caucasian ore decreased $\left(\frac{0.47}{7}\right)$=0.067 volt, the domestic ore $\left(\frac{0.56}{7}\right)$=0.080 volt, and the Brazilian ore $\left(\frac{0.45}{7}\right)$=0.64 volt.

The potential of the chemically prepared oxide appears to be independent of hydrogen ion concentration, for which no explanation is offered. This difference from the ores was entirely unexpected and requires further study.

(3) *Effect of Time:*

The increase in potential produced by increased acid concentration would suggest a simple means of increasing the voltage of a dry cell, and it has been said to have been used by dishonest makers to "boost" the voltage and "flash point" of their dry cells. It has the disadvantage, however, that the voltage drops from day to day. This is indicated by the dotted curves in Fig. 2, which represent the potentials at the end of one week. Thus it is seen that the potential gradually decreased in acid solutions and increased slightly in alkaline solutions. These results would indicate that the shelf-life[11] of a cell containing acid would probably be short, entirely apart from the action of the acid solution upon the zinc.

(4) *Relation of Hydrogen Ion Concentration and Open Circuit Voltage of Dry Cells:*

Experiments showed that the potential of a zinc electrode in the solutions corresponding to Curve V varies less than 0.02 volt, that is, the zinc potential is practically independent of the hydrogen ion concentration of the solution. But since the potential of the carbon-manganese dioxide is dependent upon the hydrogen

[11] At the beginning of this investigation it was hoped that the change in potentials over a short period of time might serve as an indication of the probable shelf-life of a dry cell containing the ore or oxide tested. The results obtained, however, were not sufficient to justify the conclusion that it is possible to predict the shelf-life of an ore by such a method.

ion concentration, the open circuit voltage of the dry cell containing a given ore is therefore determined by the hydrogen ion concentration of its electrolyte. It would be possible then to vary the open circuit voltage, when the cell is new, by 0.4 or 0.5 volt by simply adding acid or alkali to it.

Measurements of the hydrogen electrode potential in solutions containing 12.5 to 50 percent of ammonium chloride and up to 40 percent of zinc chloride gave values from 0.52 to 0.59 volt against the tenth-normal calomel electrode, corresponding to hydrogen ion concentrations from 10^{-8} to $10^{-4.5}$. Since the slope of the curves for the ores near the neutral point is much less than that for the hydrogen electrode, the variation in the open-circuit voltage caused by differences in hydrogen ion concentration of ammonium and zinc chlorides solutions would be somewhat less than 0.07 volt.

(5) *Relation of Hydrogen Ion Concentration and Polarization of a Dry Cell:*

There is no means of measuring the hydrogen ion concentration of the electrolyte in a dry cell with a hydrogen electrode. From the previous discussion it appears that the potential of the manganese dioxide electrode gives about as true a value of the hydrogen ion concentration in a dry cell as it is possible to obtain.

While it is true that zinc chloride would reduce the alkalinity produced by ammonia formed during discharge of the cell, it is probable that the alkalinity would at least amount to that represented in Curve V, that is 10^{-8}. Assuming this to be true, then the decrease in hydrogen ion concentration from that of the neutral ammonium chloride solution to about 10^{-8} would cause a drop of 0.17 volt in the voltage of a cell containing the Caucasian ore, 0.21 for the domestic ore, and 0.14 volt for the Brazilian ore. Roughly, then, a drop in voltage of at least 0.15 to 0.20 volt may be due to decreased hydrogen ion concentration. At least a portion of the polarization of a dry cell is therefore probably due to the layer of electrolyte on the surface of the electrode becoming impoverished in hydrogen ions.

To determine the relative change in potentials of the electrodes of a dry cell, during discharge, a No. 6 cell was discharged continuously through a resistance of 10 ohms, and the potentials of

the electrodes were measured at frequent intervals with a tenth-normal calomel electrode and a potentiometer (Fig. 3). It is noted that after the first 50 hours the potential of the zinc is very constant for the remaining 170 hours, while during the latter period of time the manganese dioxide electrode dropped 0.28 volt (from + 0.04 to — 0.24). From the previous discussion it is reasonable to assume that the reduced hydrogen ion concentration is responsible for 0.15 or 0.20 volt of this drop. It, however, must not be forgotten that the chemical changes (reduction of the oxide) at the surface of the electrode during discharge would also lower the potential.

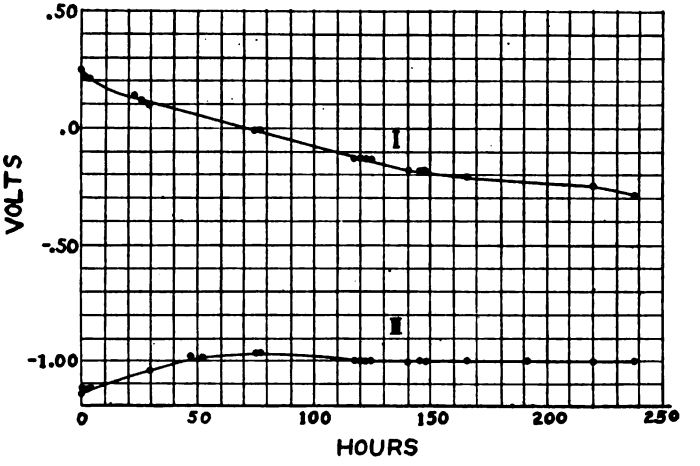

FIG. 3.

IV. CONCLUSIONS.

(1) The potential of an electrode composed of a mixture of graphite and some manganese ores is a logarithmic function of the hydrogen ion concentration of the solution in contact with the electrode.

(2) The potential of similar electrodes containing a chemically prepared oxide instead of the natural ores is independent of the hydrogen ion concentration.

(3) The potential of the natural ores steadily decreased with time in acid solutions, indicating either a consumption of hydrogen ions or a reduction of the oxide or both.

(4) The potential of the natural ores steadily but slowly increased in alkaline solutions, indicating either a consumption of hydroxyl ions or oxidation of the oxide or both.

(5) Slight variations in the hydrogen ion concentrations of solutions of ammonium chloride and zinc chloride are sufficient to account for variations of several hundredths of a volt in open-circuit voltages of dry cells containing the same ore.

(6) At least a portion of the polarization of a dry cell during discharge may be explained as being due to a layer of electrolyte on the surface of the electrode impoverished in hydrogen ions.

Washington, D. C.
Aug. 13, 1919

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920. President Bancroft in the Chair.

THE EFFECT OF AN ALTERNATING CURRENT ON HYDROGEN OVERVOLTAGE.[1]

By H. M. Goodwin[2] and M. Knobel.[3]

Abstract.

A study of the over-voltage of hydrogen on platinum, lead, and copper cathodes when alternating current is superposed on the direct electrolyzing current. The apparatus is described, the electrodes, and the manner of working. The effect of varying the alternating current was also studied, the effect of its frequency and the power factor. The effects seem in general to be due to the oxygen liberated on the cathode by the reverse wave of the alternating current. The magnitude of this depolarization appears to be independent of the electrodes and of the current density, and determined primarily by the ratio of alternating to direct current used. The effect increases slightly as the frequency decreases, but is practically independent of the power factor.

[J. W. R.]

It is well known that over-voltage is influenced by the superposition of an alternating current on the direct electrolyzing current, although the subject has not been very extensively investigated. Thus Ghosh[4] found that the electrode potential of polished platinum was decreased by an alternating current of frequency 500 cycles per second while no effect was produced with platinized electrodes. In a later paper[5] he showed that the current output of an irreversible primary cell was increased by the application of an alternating current owing to the diminution of the back

[1] Manuscript received March 13, 1920.

[2] Professor of Electrochemistry, Mass. Inst. of Technology.

[3] Instructor in Physicis, Mass. Inst. of Technology.

[4] J. Am. Chem. Soc. (1914), 36, 2333.

[5] J. Am. Chem. Soc. (1915), 37, 733.

electromotive force of polarization. The effect on reversible cells however was found to be negligible.

The effect on anodic polarization has also been noted, the polarization being in all cases apparently decreased. Thus Reitlinger[6] found the production of persulphuric acid to be decreased with application of alternating current, which indicates a decrease in anode potential, as a high potential is requisite for a yield of persulphate. In electrolyzing alcohol with platinum electrodes he obtained, with superposed alternating current, aldehyde instead of acetic acid, again indicating reduction of the anodic potential.

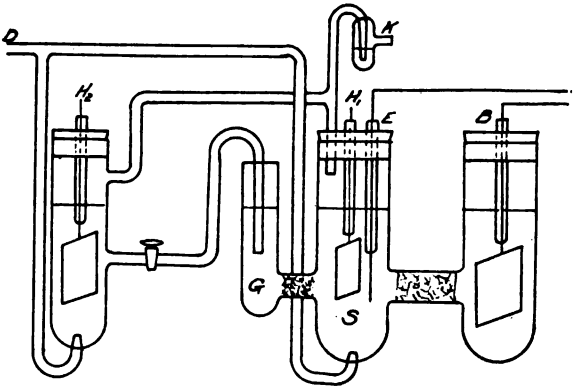

FIG. 1. Cell.

Archibald and von Wartenburg[7] observed the production of ozone to be increased when alternating current was superposed on the direct current in the electrolysis of H_2SO_4. This they explained by a reduction in anodic potential by the alternating current.

Ruer[8] carried out experiments on the solution of platinum anodes in H_2SO_4 under the action of direct and alternating currents. He explained the solution of the platinum under these conditions as essentially a chemical process involving both the hydrogen and oxygen liberated at the anode.

The specific purpose of our investigation was to ascertain the

[6] Z. f. Elektrochem. (1914), 20, 261.
[7] Z. f. Elektrochem. (1911), 17, 812.
[8] Z. f. phys. Chem. (1903), 44, 81.

effect of frequency, ratio of alternating to direct current, and alternating current power factor on the hydrogen polarization at various metallic cathodes, with special reference to the possible technical application of the results to electrolytic processes in which a reduction in over-voltage might be advantageous.

Preliminary experiments were carried out in 1915 by one of the authors in collaboration with A. R. Brooks[9] using mercury cathodes, but the work was interrupted before completion. These experiments served, however, as an introduction to the present investigation.

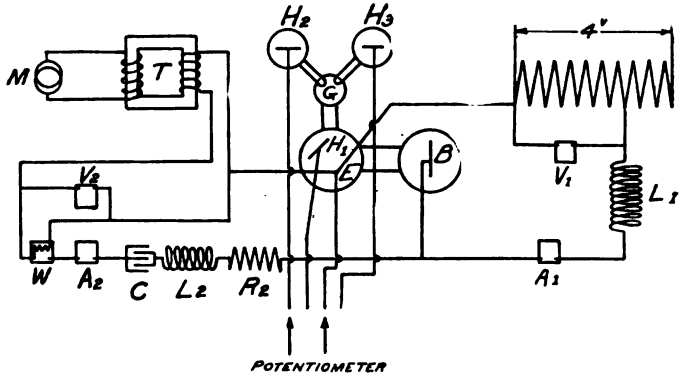

FIG. 2. Diagram of Connections.

DESCRIPTION OF APPARATUS.

The type of cell used and the diagram of connections are shown in Figs. 1 and 2. The compartment S, Fig. 1, one and one-half inches (4 cm.) in diameter, contained the electrode E to be investigated and a platinized platinum electrode H_1, which served as a reference electrode. The anode B was also of platinized platinum. The tube connecting the anode and cathode compartments was plugged with glass wool to prevent diffusion. The side arm G, which was connected with S by a tube plugged with glass wool, served to make connection with two hydrogen reference electrodes H_2 and H_3 (only one shown in figure). The electrode H_1 was only used to determine the degree of saturation of the acid in S

[9] A. R. Brooks: Thesis on the Effect of Alternating Current on Overvoltage. M. I. T., 1915.

with hydrogen. Over-voltage measurements on E were made against the electrodes H_2 and H_3. Hydrogen was introduced into the cell through D. In the outlet at K, a slight pressure, less than 5 mm. of water, was maintained to prevent diffusion of air into the apparatus.

Direct current was obtained by tapping off any desired potential from a drum rheostat connected to a 4-volt storage battery of large capacity. A rather large current was used through the rheostat to eliminate any changes in the voltage due to change of the current in the cell circuit. A_1 is a milliammeter with a range from 0 to 10 milliamperes and reading to 0.01 milliampere. V_1 is a voltmeter; L_1 is a large inductance (transformer secondary), its purpose being to prevent alternating current from entering the direct current circuit.

The alternating current was obtained from two variable-frequency generators, which allowed a variation of frequency from two to over one hundred cycles per second. The current wave form was approximately sinusoidal. The frequency could be maintained constant to one cycle per second. T is a variable ratio transformer. W, A_2 and V_2 are alternating current wattmeter, ammeter, and voltmeter respectively. These were of the dynamometer type calibrated with direct current over the desired range. C is a variable capacity and L_2 and R_2 a variable inductance and resistance respectively. With these a wide variation in power factor of the alternating current could be secured. A close regulation of the alternating current was obtained by varying the field voltage of the generator.

The over-voltage was measured by the ordinary Poggendorf method, using a capillary electrometer as indicating instrument.

The hydrogen gas for the cells was supplied from an electrolytic hydrogen generator. The gas was in all experiments first bubbled through acid of the same concentration as that in the cell.

The electrolyte was normal sulphuric acid. It was made from the purest acid obtainable without special redistillation. The same solution was used in the hydrogen electrodes H_2 and H_3. To obtain the electrode potential in terms of the normal hydrogen electrode ($2N.H_2SO_4$) a correction must be made for the differ-

ence in hydrogen ion concentration in a normal and twice normal acid solution; this correction is approximately 0.016 volt (subtractive).

All measurements were made at temperatures within one degree, and most of them within one-half degree of 25° C.

Immediately before each run the acid in the cell S was saturated with hydrogen gas, as indicated by the potential of the auxiliary electrode H_1, but the gas was not bubbled continuously through the solution during the measurements.

In obtaining the data for the curves showing the variation of polarization with increasing direct current and constant alternating current, the procedure was to increase the D. C. voltage applied to the cell by steps of about 0.1 volt and after waiting an interval of three minutes to measure the over-voltage and current. This interval was found to be sufficiently long for the electrode potential to become sensibly constant. Where other factors were varied, the procedure was in general the same, exactly three minutes being allowed to elapse in every case before the over-voltage was recorded.

ELECTRODES.

The metals chosen for cathodes were polished platinum, electrolytically deposited lead, mercury and copper. The last two metals were found to give unsatisfactory results and were rejected as unsuitable for our work.

All the platinum electrodes used in the runs were made of pure polished wire sealed into glass tubes.

In addition to the platinum, which shows a relatively low over-voltage, it was thought desirable to select another metal having a high over-voltage in order that the effect of the superposed alternating current might be as large as possible. Further the metal should be one on which the over-voltage is reasonably constant and the magnitude of which is quickly established. Mercury was first tried, but was found to give results altogether too uncertain. This is in accord with the experience of Brooks in the preliminary work on this research and of others, in particular Lewis and Jackson,[10] who found that even after three months reproducible measurements could not be made with this metal.

[10] Proc. Am. Acad. (1906), **41**, 399.

Copper electrodes were also investigated but the surface became in time so changed under the action of the alternating current as to give unreliable results. Only one run with this electrode was made.

TABLE I *A*.

Curve *A*, Fig. 3; lead electrode plated at 9.0 milliamperes per square centimeter; area 0.23 sq. cm.

Current	Overvoltage	Current	Overvoltage
0.00	0.264	1.00	0.660
0.01	0.344	2.10	0.707
0.06	0.441	4.50	0.756
0.15	0.530	7.60	0.770
0.40	0.592		

TABLE I *B*.

Curve *B*, Fig. 3; lead electrode plated at 7.0 milliamperes per sq. cm.; area 0.342 sq. cm.

Current	Overvoltage	Current	Overvoltage
0.00	0.352	0.005	0.660
0.00	0.396	0.10	0.728
0.00	0.455	0.45	0.790
0.005	0.504	1.55	0.835
0.005	0.564	3.90	0.865
0.005	0.612	7.00	0.889

TABLE I *C*.

Curve *C*, Fig. 3; lead electrode plated at 3.2 milliamperes per sq. cm.; area 0.363 sq. cm.

Current	Overvoltage	Current	Overvoltage
0.00	0.660	1.80	0.926
0.03	0.745	3.50	0.985
0.28	0.808	5.40	1.03
0.83	0.876	9.50	1.09

TABLE I *D*.

Curve *D*, Fig. 3; lead electrode not plated with lead; area 0.60 sq. cm.

Current	Overvoltage	Current	Overvoltage
0.00	0.564	0.35	1.027
0.01	0.66	1.30	1.075
0.01	0.754	3.80	1.112
0.05	0.856	6.25	1.140
0.08	0.948	9.60	1.165

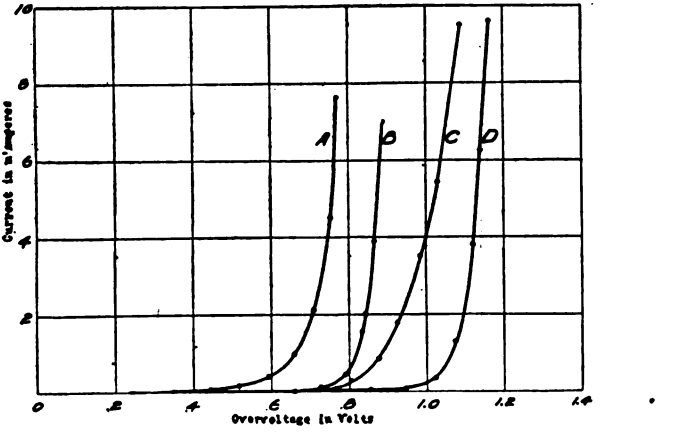

FIG. 3. Overvoltage Current Curves for Lead Electrodes plated at different current densities, showing effect of roughness of surface.

Lead, however, was found to give very satisfactory and concordant results. The electrodes were made of square sections of commercial lead, approximately 0.35 square centimeter in area, held in glass tubes by sealing wax. They were plated electrolytically with lead from a bath of pure lead perchlorate.

An interesting confirmation of the variation of over-voltage with the condition of the metal surface was obtained in the preliminary measurements with lead. The roughness of the surface depended on the current density with which the lead was deposited. In Fig. 3 (data given in Tables I*A*, I*B*, I*C* and I*D*) the over-voltage-current curves are plotted for four electrodes. The ordinates are values of the electrolyzing current in milli-

amperes and the abscissae the directly measured difference in potential (over-voltage) between the lead electrode E and the hydrogen electrode H_2 (Fig. 1). The data for the four runs were taken under strictly comparable conditions.

TABLE II.

Preliminary alternating current measurements.
Data plotted in Fig. 4.

A.C./D.C. 1.77. D.C. 2.00 m.a. (C.D. 6.4 m.a./sq. cm.)
A.C. 3.50 m.a. (C.D. 11.2 m.a./sq. cm.)

Power factor 1.0. Frequency 60 cycles.
Platinum wire electrode, area 0.312 sq. cm.

Time	Overvoltage	Time	Overvoltage
0	0.133	14	0.146
2	0.128	15	0.136
3 AC off		16	0.136
3-10	0.268	17	0.134
3-30	0.280	17-30 AC off	
4-10	0.296	17-45	0.264
5	0.311	18	0.276
6	0.343	22	0.349
8	0.363	22-30 AC on	
8-10 AC on		22-45	0.146
8-30	0.142	23-30	0.138
9-10	0.128	23-45 AC off	
10	0.132	24	0.272
12	0.132	27	0.333
12-30 AC off		27-30 AC on	
12-40	0.260	28	0.142
12-50	0.272	28-15 AC off	
13-30	0.288	28-30	0.274
13-40 AC on		29 AC on	0.142

Curve A shows the results with an electrode on which the lead was plated with a current density of 9.0 milliamperes per square centimeter. It was very rough and somewhat resembled the surface of gas carbon. Data shown in curve B were obtained with an electrode plated with a current density of 7.0, and data in curve C with an electrode plated with a current density of 3.2 milliamperes per square centimeter respectively. The latter electrode showed a beautiful, rather smooth, white deposit. Values

shown in curve *D* were obtained with an unplated electrode, the surface of which was made quite smooth by careful scraping. The graphs bring out clearly the fact that the rougher the surface of the electrode the lower is the cathodic polarization for a given current at high as well as low current densities. The decomposition potential as indicated by the first visible bubble evolution (Caspari), as seen under a reading glass, was found to depend less upon the roughness of the surface than the above curves

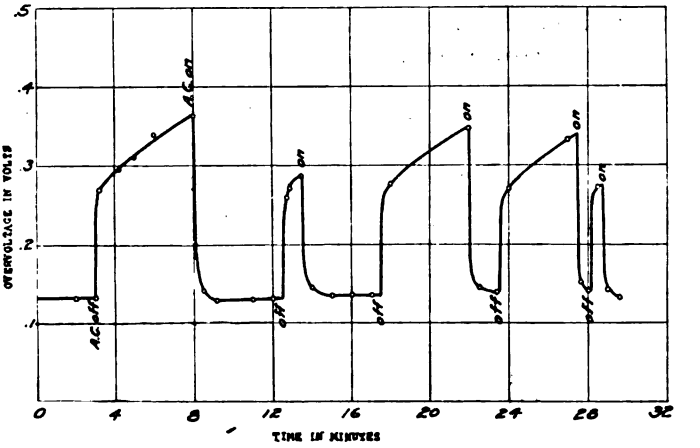

FIG. 4. Showing typical effect of alternating current on overvoltage.

would indicate, the average value of eighteen runs with eight electrodes (varying from the smoothest to the roughest) being 0.48 ± 0.04 volt.

EFFECT OF SUPERIMPOSED ALTERNATING CURRENT ON HYDROGEN POLARIZATION.

The general effect resulting from the simultaneous action of an alternating and a direct current on the polarization of hydrogen is well illustrated by the data in Table II shown in Fig. 4. The conditions of the experiment were as follows: The cathode was polished platinum wire 0.312 square centimeters in area. The direct current voltage was first increased until a steady current of 2.00 milliamperes was established through the cell. An alternating current of 60 cycles and 3.50 milliamperes was then

imposed on the circuit and the value of the polarization at the platinum electrode measured against the constant reference electrode. The value was 0.130 volt. The alternating current was then switched off and the polarization instantly increased, thereby

TABLE III *A*.

Data plotted in Curve *A*, Fig. 5.

Varying alternating current with constant direct current equal to 2.00 m.a. (C.D. 6.4 m.a./sq. cm.)

Power factor 1.0. Frequency 23 cycles.

Platinum electrode, area 0.312 sq. cm.

Alternating Current	Overvoltage	Alternating Current	Overvoltage
4.00	0.074	D. C. only	0.360
D. C. only	0.364	16.0	—0.101
8.	—0.020	60.0	—0.50

TABLE III *B*.

Data plotted in Curve *B*, Fig. 5.

Varying alternating current with constant direct current equal to 2.00 m.a. (C.D. 6.4 m.a./sq. cm.)

Platinum electrode, area 0.312 sq. cm.

Power factor 0.10 leading. Frequency 60 cycles.

Alternating Current	Overvoltage	Alternating Current	Overvoltage
4.00	0.093	14.0	—0.022
3.50	0.130	16.1	—0.031
4.00	0.110	18.0	—0.033
6.15	0.045	20.5	—0.051
7.90	0.037	24.1	—0.065
10.0	0.004	60.0	—0.398

cutting down correspondingly the current through the cell. This was readjusted as quickly as possible to its original value, 2.00 milliamperes, and the over-voltage again read. (This adjustment could be made within about 20 seconds). The value is seen to increase with the time, as is to be expected since an equilibrium value is not reached inside of several hours. On again applying

the alternating current the value drops rapidly and within two minutes has attained its original value of 0.13 volt. The phenomenon repeats itself with great regularity every time the alternating current circuit is opened and closed.

The minimum polarization value of 0.13 volt observed under the simultaneous action of the two currents was found to be very characteristic and easily reproducible, as is seen from the curve.

We therefore chose as the basis for discussion in our subsequent work the characteristic depressed voltage resulting from the combined alternating and direct current effects, rather than the fractional (or percentage) decrease in polarization which resulted from applying the alternating current.

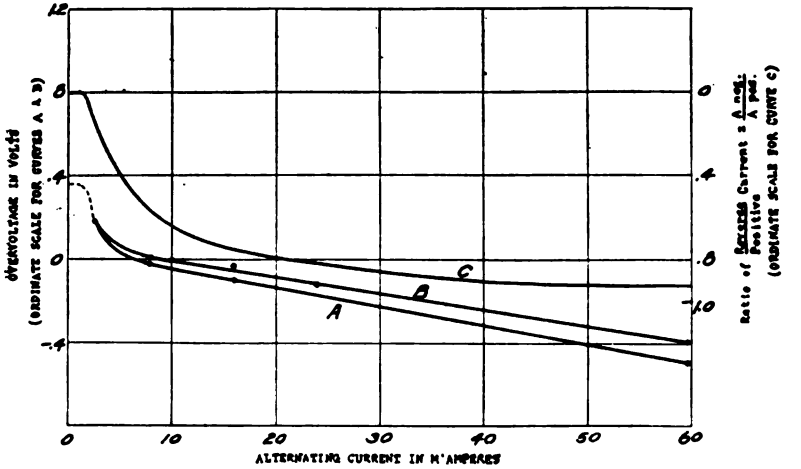

FIG. 5. Curves A and B, Overvoltage-current curves with constant D.C. of 2.00 milliamperes. Curve C, calculated curve.

EFFECT OF VARIATION OF THE RATIO OF ALTERNATING TO DIRECT CURRENT ON POLARIZATION.

The effect of gradually increasing the alternating current while maintaining the direct current constant was next investigated. This was tried with both platinum and lead electrodes. The results with platinum electrodes are shown in Tables III*A* and III*B* and in curves *A* and *B* of Fig. 5. The direct current was in all cases 2.00 milliamperes. The alternating current was varied from 2 to 60 milliamperes. As data were not obtained with A. C.

currents less than 2 milliamperes, the dotted portion of the curve is drawn as suggested from the results with lead electrodes and from theoretical calculations. See page 627. The data shown in *A* were obtained with a power factor equal to 1.0 and an alternating current frequency of 23 cycles. For the data shown in *B* the power factor was 0.1, leading, and the frequency 60 cycles.

TABLE IV *A*.

Data plotted in Curve *A*, Fig. 6.

Varying alternating current with constant direct current of 2.00 m.a. (C.D. 5.64 m.a./sq. cm.)

Power factor 1.0. Frequency 40 cycles.

Lead electrode, plated with lead, area 0.355 sq. cm.

Alternating Current	Overvoltage	Alternating Current	Overvoltage
1.55	1.038	8.3	1.060
2.05	1.014	9.4	0.640
2.90	0.984	11.8	0.621
3.6	0.890	14.1	0.594
4.7	0.790	19.4	0.572
6.3	0.707	22.6	0.554
8.3	0.655	D. C. only	0.536
D. C. only	0.627		1.048

A. C. corrected for loss in D. C. circuit.

TABLE IV *B*.

Data plotted in Curve *B*, Fig. 6.

Varying alternating current with constant direct current of 4.00 m.a. (C.D. 11.3 m.a./sq. cm.)

Power factor 1.0. Frequency 40 cycles.

Lead electrode, plated with lead, area 0.355 sq. cm.

Alternating Current	Overvoltage	Alternating Current	Overvoltage
D. C. only	1.070	9.4	0.706
2.6	1.065	11.8	0.689
3.7	1.035	16.2	0.655
4.8	0.922	21.1	0.625
5.6	0.861	D. C. only	1.070
7.1	0.777		

A. C. corrected for loss in D. C. circuit.

TABLE IV *C*.

Data plotted in Curve *C*, Fig. 6.

Varying alternating current with constant direct current of 8.00 m.a. (C.D. 22.6 m.a./sq. cm.)

Power factor 1.0. Frequency 40 cycles.

Lead electrode, plated with lead, area 0.355 sq. cm.

Alternating Current	Overvoltage	Alternating Current	Overvoltage
D. C. only	1.105	9.4	0.912
4.0	1.098	11.8	0.825
5.6	1.080	16.2	0.770
7.1	1.040	21.8	0.734
8.3	0.970	D. C. only	1.138

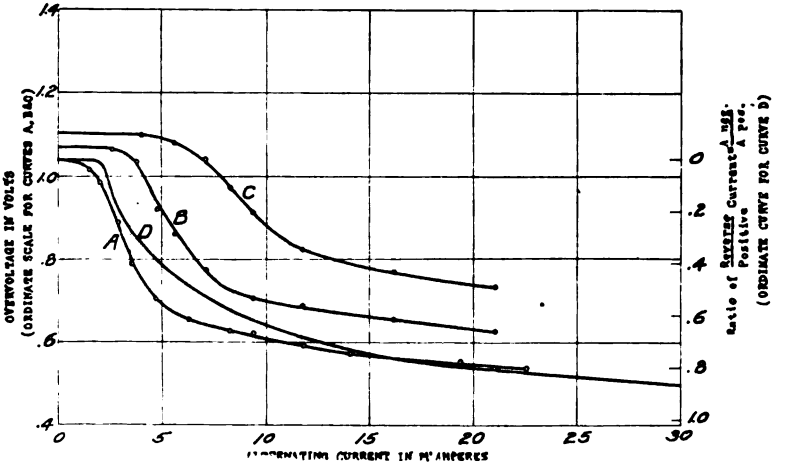

FIG. 6. Curves A, B and C, Overvoltage-current curves with constant D.C. Curve D, calculated curve.

The results indicate in both cases a rapid decrease in polarization as the alternating current is first applied; the decrease becomes approximately proportional to the ratio of alternating to direct current for higher values. In fact, for large values, the polarization becomes negative indicating that hydrogen is evolved more readily than on a reversible electrode. These relations are further well illustrated in Curves *A*, *B* and *C* in Fig. 6 (Data in Tables IV*A*, IV*B* and IV*C*) obtained with lead electrodes. In these

curves the constant direct current was 2, 4, and 8 milliamperes respectively, thus giving slightly different initial values for the polarization with no alternating current. The sudden falling off of the polarization due to the impressed alternating current begins later the greater the value of the direct current, but the general form of the curve is the same in all cases. The drop in polarization is, in other words, determined primarily by the *ratio* of

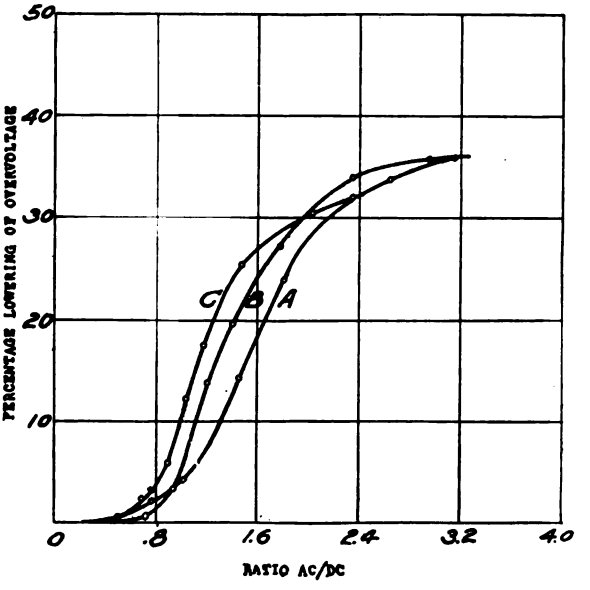

FIG. 7. Ratio AC/DC with constant D.C. plotted against percentage lowering of overvoltage for data in Fig. 6.

alternating to direct current rather than by the absolute value of the alternating current. This is shown more clearly in Fig. 7, where the percentage lowering in polarization produced by a given alternating current is plotted against the corresponding ratio of the currents for the three curves *A*, *B* and *C*, of Fig. 6. It is seen in each case that the polarization is not sensibly affected until the ratio of alternating to direct current reaches a value approximately $1/\sqrt{2} = 0.7$. The magnitude of the effect is then approximately the same for all three cases although the direct current

varied from 2 to 8 milliamperes. As the electrodes were identical in all these experiments, the direct current density varied also in the same ratio, hence the effect under consideration is not determined by this factor.

TABLE V *A*.

Data plotted in Curve *A*, Fig. 9.
Constant direct current 2.00 m.a. (C.D. 6.25 m.a./sq. cm.)
Constant alternating current 10.0 m.a. (C.D. 31.2 m.a./sq. cm.)
Power factor 1.0.
Platinum electrode, area 0.32 sq. cm.

Frequency	Overvoltage	Frequency	Overvoltage
100	0.000	22.5	—0.016
90	0.000	17.5	—0.034
70	—0.008	15	—0.030
59	—0.008	10	—0.010
42	—0.006	2.9	—0.02 (uncertain)
30	—0.012		

TABLE V *B*.

Data plotted in Curve *B*, Fig. 9.
Constant direct current 2.00 m.a. (C.D. 6.25 m.a./sq. cm.)
Constant alternating current 10.0 m.a. (C.D. 31.2 m.a./sq. cm.)
Power factor 1.0.
Platinum electrode, area 0.32 sq. cm.

Frequency	Overvoltage	Frequency	Overvoltage
23	—0.060	60	—0.002
30	—0.044	75	0.00
40	—0.030	90	0.002
50	—0.024	100	0.012

The decrease in polarization produced by an alternating current is also well shown by the usual current-voltage decomposition curves, with alternating currents of constant value superposed upon the electrolyzing current. Three such curves are shown in Fig. 8 in which the alternating current had values of 2, 4, and 10

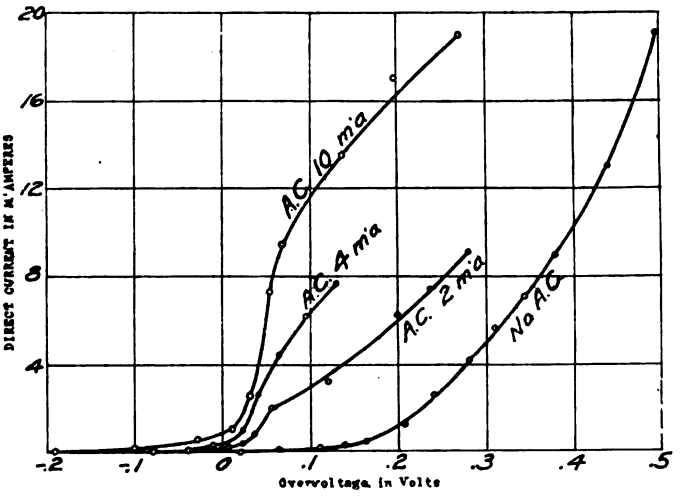

FIG. 8. Overvoltage current curves with constant A. C. current.

TABLE VI.

Data plotted in Fig. 10.
Constant direct current 2.00 m.a. (C.D. 5.64 m.a./sq. cm.)
Constant alternating current 10.0 m.a. (C.D. 28.2 m.a./sq. cm.)
Power factor 1.0.
Lead electrode, plated with lead, area 0.355 sq. cm.

Frequency	Overvoltage	Frequency	Overvoltage
100	0.621	32	0.600
90	0.629	37.5	0.600
75	0.624	46	0.601
58	0.609	61	0.608
46	0.599	75	0.624
30	0.596	90	0.642
22.5	0.606	100	0.646
22.5	0.603		

milliamperes respectively, a frequency of 23 cycles and power factor unity. The results are in entire agreement with those previously discussed. As the direct current increases in value the curves approach that for which the alternating current is zero; the approach is the more rapid the smaller the value of the alternating current. This agrees with the results shown in Fig. 6,

where it was found that for very small values of the ratio of alternating to direct current the effect of the alternating current became negligible.

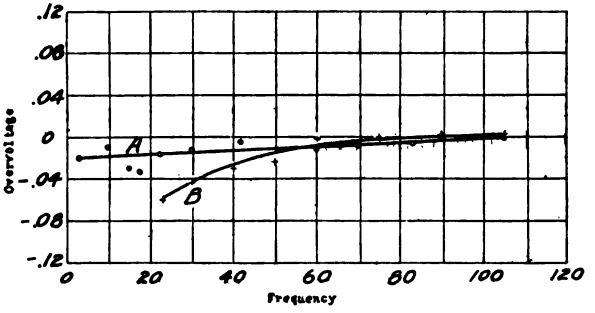

FIG. 9. Showing change of overvoltage with frequency at platinum electrode.

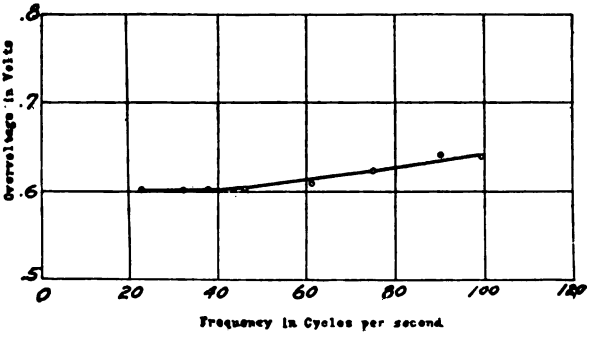

FIG. 10. Showing change of overvoltage with frequency at lead electrode.

EFFECT OF FREQUENCY.

It is well known that decreasing the frequency of an alternating current increases, in general, its electrolytic effect. If, therefore, the depolarizing action of the current found in the above experiments is due to alternating current electrolysis, the effect should be greater for low than for high frequencies. This was found to be the case by Brooks in his measurements with mercury cathodes and is confirmed by our measurements with both lead and platinum electrodes. The effect is not very great however, as is evident from the curves in Fig. 9 (data in Tables V *A* and

V *B*). In obtaining the data for these curves, the direct and alternating currents and power factor were all maintained constant, the only variable condition being the frequency. This was measured with a frequency meter for frequencies down to 22.5 cycles, below which it was calculated from the speed of the generator determined by a revolution counter. The electrodes were made of platinum.

Another series of similar data using lead electrodes are plotted in Fig. 10 (data in Table VI).

TABLE VII *A*.

Data plotted in Curve *A*, Fig. 11.
Constant direct current 2.00 m.a. (C.D. 6.25 m.a./sq. cm.)
Constant alternating current 6.75 m.a. (C.D. 29.6 m.a./sq. cm.)
Frequency 40 cycles.
Platinum electrode, area 0.32 sq. cm.

Power Factor	Overvoltage	Power Factor	Overvoltage
0.48 lag	0.041	0.81 lead	0.053
0.54 "	0.045	0.48 "	0.063
0.94 "	0.047	0.19 "	0.042
0.98 "	0.047	0.026 "	0.062

TABLE VII *B*.

Data plotted in Curve *B*, Fig. 11.
Constant direct current 2.00 m.a. (C.D. 6.25 m.a./sq. cm.)
Constant alternating current 20.0 m.a. (C.D. 62.5 m.a./sq. cm.)
Constant frequency 60 cycles.
Platinum electrode, area 0.32 sq. cm. (not the same as in Curve *A*).

Power Factor	Overvoltage	Power Factor	Overvoltage
0.45 lag	—0.0355	0.33 lead	—0.0091
0.55 "	—0.0297	0.23 "	0.00
0.83 "	—0.0334	0.04 "	0.010
1.0 "	—0.0334	0.02 "	0.010
0.78 lead	—0.0334	0.016 "	0.012
0.45 "	—0.0234		

TABLE VIII.

Computed value of ratio $\frac{\text{Total coulombs liberating oxygen.}}{\text{Total coulombs liberating hydrogen.}}$

Direct Current = 1.00 = Const. Alternating Current (root-mean-square)	Coulombs for Oxygen $A_{negative}$	Coulombs for Hydrogen $A_{positive}$	Ratio $\frac{A_{negative}}{A_{positive}}$
0.707	0.00	6.283	0.00
1.00	0.4292	6.713	0.0639
1.414	1.370	7.654	0.179
2.00	2.880	9.160	0.318
4.00	8.360	14.64	0.570
8.00	19.59	25.87	0.756
16.00	42.16	48.44	0.872
30.00	81.90	88.18	0.927

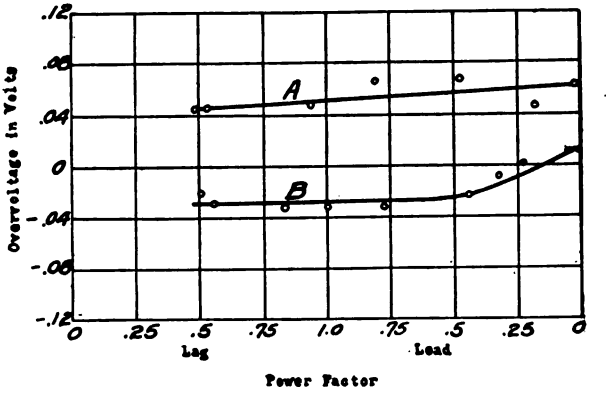

FIG. 11. Variation of overvoltage with power factor with constant D.C. and A.C.

EFFECT OF POWER FACTOR.

So far as we know, the relation between over-voltage and power factor has not been previously investigated. Reitlinger[11] found in some experiments in alternating current electrolysis that the effect of the current was diminished with higher frequencies. He stated this was caused by the greater phase displacement between the voltage and the current, due to greater capacity reactance of

[11] Z. f. Elektrochem. (1914), **20**, 261.

the electrode, but gave no reason why change in power factor itself should affect the over-voltage. A similar statement was made by Rothmund[12] in connection with an electrolytic detector.

The following experiments were carried out with platinum cathodes. Both alternating and direct currents and the frequency were maintained constant while the power factor was varied. The power factors were determined by the meters already described,

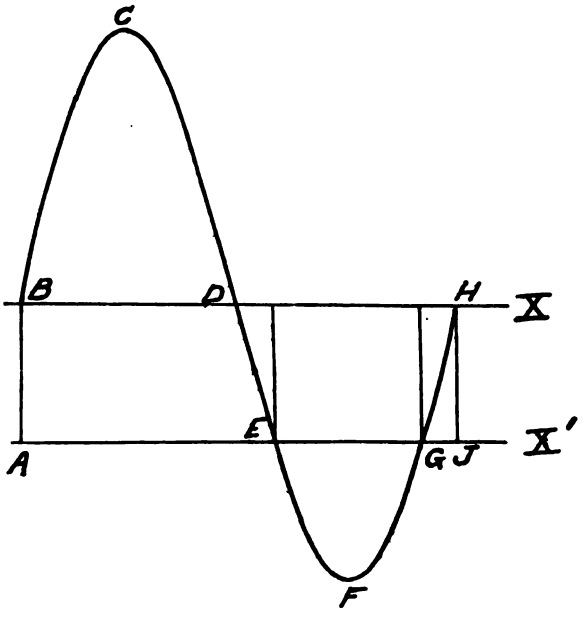

FIG. 12.

except for the lowest values. Here the necessarily high voltage was too great for the dynamometer, but a 150-volt 1 ampere compensating wattmeter gave a sufficient indication to permit of an approximate estimate of the value of the power input.

In Fig. 11 (data in Tables VII *A* and VII *B*) two runs are plotted. *A* was taken with a direct current of 2.00 milliamperes, alternating current of 6.75 milliamperes and frequency of 40 cycles. *B* was with direct current of 2.00 milliamperes, alter-

[12] Drude's Ann. (1904), **15**, 193.

nating current of 20 milliamperes and frequency of 60 cycles. It appears from the curves that the power factor has very little effect. The curves are plotted with a large scale of ordinates, which apparently magnify the variations found. Assigning equal weight to all observations, the variations in curve *A* fluctuate only about 0.01 volt from the mean value over a range of power factor from 0.6 lag to nearly zero lead. In series *B*, in which the ratio of alternating to direct current is greater, the effect is practically zero from 0.5 lag to 0.4 lead. As the lowest values of the power factor are subject to considerable error owing to the insufficient range of the measuring instruments, we place less weight upon them.

The general conclusion to be drawn from the above measurements is that the depolarizing action of an alternating current is practically independent of its power factor.

DISCUSSION OF RESULTS.

The action of the alternating current appears to be due to the oxygen liberated at the cathode by the reverse current. The ratio of the theoretical quantity of oxygen evolved to that of hydrogen can be calculated as follows: Assuming a sinusoidal wave form for the alternating current, the resultant wave form with direct current will be sinusoidal. When a direct current of magnitude XX' is combined with an alternating current the effect is to lower the axis of zero current of the latter from BX to AX', see Fig. 12. The area $ABCDE$ plus the area GHJ gives the coulombs per cycle passing in the direction of the direct current, and the area EGF gives the coulombs passing in the opposite direction. The expressions for these areas can be shown to be

$$A_{\text{positive}} = \pi + 2\sqrt{I_m^2 - 1} + 2\,Sin^{-1}\frac{1}{I_m},$$

$$A_{\text{negative}} = 2\sqrt{I_m^2 - 1} - \pi + 2\,Sin^{-1}\frac{1}{I_m}$$

respectively, where I_m is the maximum value of the alternating current.

In Table VIII are given the computed values from which curve *C*, Fig. 5, and curve *D*, Fig. 6, are plotted. The ordinate scale of these curves,

$$\text{Ratio of } \frac{A_{\text{negative}}}{A_{\text{positive}}},$$

is given on the right-hand side of the figure. The corresponding abscissæ chosen are twice the values of the alternating current in column 1 as the data plotted in the curves, Fig. 5, and in *A*, Fig. 6, were obtained with D.C. currents twice the magnitude of that assumed in calculating the table.

From the similarity of the experimentally determined curves *A* and *B*, and the calculated curve *C* in Fig. 5, and the experimental curves *A*, *B*, and *C*, and the calculated curve *D* in Fig. 6, it appears probable that the reduction in over-voltage is due to the depolarizing action of the oxygen. No effect is observed until the alternating current is large enough to cause some reverse current to pass through the cell, and the rapid decrease in over-voltage which then follows corresponds closely with the quantity of oxygen theoretically liberated.

If the depolarization results from a direct chemical reaction between the liberated oxygen and the hydrogen, the small observed change of polarization with frequency would indicate a high velocity for the reaction. It would be interesting to extend these experiments to very high frequencies.

If the depolarization, as appears from the above considerations, is due to the liberated oxygen, which is proportional to the reverse current, it would be expected that the power factor of the alternating current would have no effect upon the polarization, as was found to be the case. The depolarization is determined by the value of the currents only, and not by the alternating electromotive force.

SUMMARY.

1. An alternating current superposed on a direct current lowers the cathodic polarization of hydrogen. The effect was studied with platinum, lead and copper cathodes.

2. The magnitude of the depolarization is determined primarily by the ratio of alternating to direct current, and appears to be independent of the electrodes and of the current density.

3. The effect varies slightly with frequency, the tendency being to increase as the frequency is diminished. For a variation of frequency from 2 to 100 cycles, the depolarization increased only about 50 millivolts.

4. The effect is practically independent of power factor, varying less than 30 millivolts for a change in power factor from 0.5 lag to nearly zero lead.

5. The depolarization is shown to be probably due to the action of the liberated oxygen on the hydrogen.

Rogers Laboratory of Physics,
Electrochemical Division,
Massachusetts Institute of Technology.

DISCUSSION.

E. O. BENJAMIN[1]: Were the heating effects of the alternating current taken into account?

M. KNOBEL: This work is done at room temperature, at a temperature of about 25 degrees, and the variation is not more than a degree; the currents are comparatively small, I do not believe there is any error due to that.

E. O. BENJAMIN: Invariably there is a local heating on the electrode surface due to the alternating current.

M. KNOBEL: That may be, I could not say.

E. O. BENJAMIN: That would be dissipated throughout the electrode.

M. KNOBEL: Yes.

D. F. CALHANE[2]: We also find that the effect of current density on the oxidation at the anode is quite a factor and frequency also affects the result.

C. N. RICHARDSON (*Communicated*): The authors' curve between power-factor and overvoltage indicates a negligible power-factor effect. However, according to the diagrams, the power-

[1] Chief Chemist and Engineer, International Oxygen Co., Newark, N. J.
[2] Professor of Electrochemistry, Worcester, Mass.

factor of the whole circuit (a. c.) was changed by varying C, L_2, and R_2. This obviously has no effect on the power-factor of the cell itself, and the curve therefore has no meaning.

The power-factor of the cell is fixed by the constants of the cell, and cannot be changed without changing those constants. Therefore the reason there was no appreciable effect due to power-factor is that the power-factor of the cell was not changed.

H. M. GOODWIN (*Communicated*): Mr. Richardson is, of course quite right in stating that the power-factor across the cell may remain constant while that of other parts of the circuit are varied. As measured in the above experiments the values given are for the power-factor of the circuit as a whole.

It would be of interest to make an oscillograph study of the current voltage relations within the cell, as Scott's measurements on "polarization capacity" indicate that very material capacities exist at platinum electrodes during electrolysis, which would tend to cut down the power-factor in the cell. This method was applied by LeBlanc to a study of polarization phenomena in 1910.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

THE REACTIONS OF THE LEAD ACCUMULATOR.[1]

By D. A. MacInnes, L. Adler and D. B. Joubert.

ABSTRACT.

An experimental study of the amount of sulphuric acid consumed during the discharge of a lead accumulator, in order to determine whether two or one gram equivalents of acid disappear per Faraday passing, in order to decide between Gladstone and Tribe's formula for the chemical reaction or that advanced by Fèry. The results were intermediate of the two. Careful chemical analyses of the oxide formed during charging show it to be certainly PbO_2. The chemical potential of the oxide on the positive plate was also found identical with that of chemically prepared PbO_2 and electrically precipitated PbO_2. It is suggested tentatively that intermediate oxides, such as Pb_3O_4, or basic compounds, such as $(PbO)_x . PbSO_4$ may be formed during discharge.

[J. W. R.]

1. INTRODUCTION.

The equation for the fundamental reaction of the lead accumulator is usually written as follows:

$$PbO_2 + Pb + 2H_2SO_4 \leftrightarrows 2PbSO_4 + 2H_2O \qquad (1)$$

The theory of the operation of the cell which is represented by this equation was first suggested by Gladstone and Tribe,[2] and has been ably supported by Dolezalek.[3] According to this "double sulphate" theory the fully-charged positive plate consists of lead peroxide, which, during discharge, is changed to lead sulphate.

[1] Contributions from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 124, and from The Chemistry Department, University of Illinois. Manuscript received March 5, 1920.

[2] "The Chemistry of the Secondary Batteries of Plante and Faure," Macmillan, 1883.

[3] "The Theory of the Lead Accumulator." Trans. by Von Ende.

The negative plate, which is formed from spongy lead, is also converted into lead sulphate while the cell is delivering energy. Fèry[4] has, however, recently proposed another explanation of the action of the cell, which may be expressed in brief form by the following equation:

$$Pb_xO_y + Pb + H_2SO_4 = PbSO_4 + zPbO_2 + H_2O, \quad (2)$$

in which Pb_xO_y is a higher state of oxidation than PbO_2, the latter oxide appearing as a product of the discharge rather than a component of the fully-charged cell. In support of his theory, Fèry maintains (*a*) that the amount of acid used during discharge is exactly half the quantity called for by the double sulphate theory, (*b*) that there is evidence of the presence, in the active substance of a positive plate, of a higher state of oxidation of lead than is represented by PbO_2, (*c*) that an electrode composed of PbO_2, in sulphuric acid, will not produce the potential toward a reference electrode of a positive plate. As the subject is one of considerable importance, it has seemed desirable to investigate the reactions of the lead storage cell with the purpose of confirming or disproving Fèry's conclusions, especially as previous investigations have, in a number of cases, led to contradictory results.

2. THE CHANGE OF SULPHURIC ACID CONCENTRATION DURING THE ACTION OF A LEAD ACCUMULATOR.

It will be observed that the double-sulphate theory calls for two equivalents of acid for every Faraday equivalent of current which passes through a cell during discharge, whereas Fèry's theory requires just half that amount, as he points out in his papers. As this change of acid density seemed to be the method of testing these two theories which is capable of the most accurate experimental work, the following experiments were undertaken:

Two small accumulators,[5] each containing one positive and one negative plate, were given a prolonged charge. The plates were then removed, washed thoroughly with frequent changes of distilled water for 48 hours, and dried at 110° C. The plates were next returned to the vessels and a carefully weighed amount of sulphuric acid of known composition was added to each cell.

[4] Lumière Élèct. (1916), 34, 305; J. Physique (1916), 6, 21.

[5] Type BT, made by the Electric Storage Battery Co.

After several preliminary charges and discharges, during which the cells were not allowed to gas, the change of composition of the electrolyte was determined during periods in which a carefully measured quantity of electricity was drawn from the cells. The electrical connections are shown in Fig. 1. The cells I and II were connected in series with the Kelvin adjustable resistance, R_1 and the standardized resistance, R_2, to the terminals of which was connected a potentiometer. R_2 of 0.6414 ohms, which was

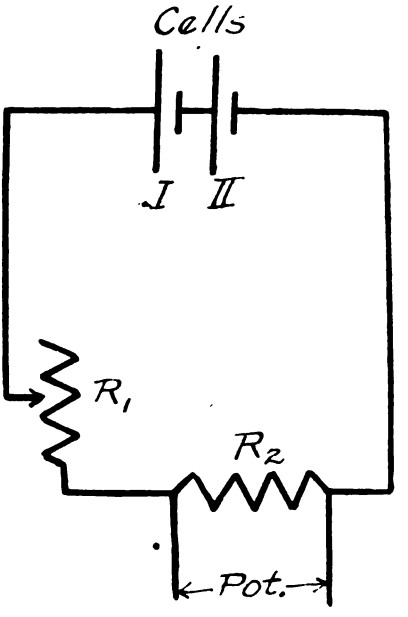

FIG. 1.

made for carrying relatively large currents without variation of resistance, was formed from coils of constantan ribbon immersed in oil. The latter and the potentiometer were carefully calibrated in connection with another research.[6] By setting the potentiometer at 0.6414 volts, for instance, the galvanometer indicated a null point when 1 ampere was passing through the circuit. Variations of the discharge current could be immediately corrected by adjustment of R_1. The composition of the acid before and after

[6] MacInnes and Braham, J. Am. Chem. Soc. (1917), 39, 2110.

discharge was determined by accurate measurement of the densities of the solutions, at 25°, and interpolation using the data given in Landoldt and Bornstein. The pycnometers had capacities of about 25 cc., and densities were readily determined to 1/100 percent. The density measurements were made several hours after the discharge, and, in several cases, were redetermined after the lapse of several more hours, with practically identical results, showing that ample time had been allowed for diffusion from the pores of the plates, and also that the results were not affected by "local action" while the cell was at rest.

The number of equivalents of acid consumed or liberated per Faraday equivalent of current we will term ϕ. Let W represent the weight of the electrolyte, and p and q the percentages ($\times$ 0.01) of H_2SO_4 at the beginning and at the end of a determination, c and F the number of coulombs and the Faraday equivalent (96,500 coulombs) respectively. Then $49\phi c/F$ and $9\phi c/F$ are the amounts of H_2SO_4 consumed and of water formed during a discharge. The percentage of H_2SO_4, q, at the end of the discharge will thus be

$$(Wp - 49c\phi/F)/(W\ [1.00 - p] + 9c\phi/F + Wp - 49c\phi/F)$$

Solving for ϕ we obtain

$$\phi = \frac{WF\ (p - q)}{c\ (49 - 40q)} \qquad (3)$$

Table I, which is largely self-explanatory, gives the data for a series of discharges of the cells.

TABLE I.

Cell	Density		Percent H_2SO_4		Weight of Acid	Coulombs	Amperes	ϕ
	Beginning	End	Beginning	End				
I	1.22728	1.22088	31.50	30.72	397.60	5,400	1	1.51
II	1.22340	1.21681	31.02	30.22	384.58	5,400	1	1.49
I	1.25487	1.25123	34.39	33.95	402.85	3,600	1	1.34
II	1.24753	1.24388	33.51	32.87	375.85	3,600	1	1.79
I	1.22880	1.21585	31.68	30.08	376.05	10,800	2	1.43
II	1.21566	1.19979	30.11	28.11	362.25	10,800	2	1.69

A similar investigation has recently been carried out by Mr. E. R. Smith, of the Massachusetts Institute of Technology. In this latter work the potentiometer and resistance were replaced by a copper coulometer. The acid concentrations were determined with the aid of the complete density tables at 20° as compiled by the U. S. Bureau of Standards, Publication 19. The values of ϕ found ranged from 1.7 to 1.8.

It will be seen that the results confirm neither the "double sulphate" theory nor the more recent explanations of Fèry, the average value of ϕ being about half way between the values required by the two theories. The work of W. Kohlrausch and C. Heim,[7] which is most frequently quoted in this connection, led to the value $\phi = 2$. Their densities were, however, made with a hydrometer, no mention being made of temperature control. Earlier work by Schenk and Farbaky[8] and by Pfaff[9] has come to our attention. These investigations led to values of $\phi = 1.50$ and 1.36 respectively. Schenk and Farbaky determined the acid concentrations by titration with alkali.

In conclusion, then, it appears that ϕ varies between 1.3 and 1.8, but is less than 2.

3. REACTIONS OF THE POSITIVE ELECTRODE.

Since the work described in the preceding section failed to enable us to decide between the "double sulphate" theory and Fèry's explanation, it became necessary to investigate further the reactions of the accumulator. As the results obtained were what would be expected if Reactions 1 and 2 took place simultaneously, it became important to determine whether any of the higher oxide postulated by Fèry is present in the positive plate.

M. A. Hollard[10] found that the lead content of the oxide deposited on a platinum anode from a solution of a lead salt is lower than would be expected if the oxide were PbO_2. Instead of the theoretical value 0.866, Hollard found values from 0.740 to 0.850. Later, using a roughened electrode, he obtained the fairly constant value 0.853. These results would follow from the presence of an oxide higher than PbO_2 or from a hydrated form of this oxide.

[7] Electrochemische Zeit. (1889), **10**, 327. (Not the better known F. Kohlrausch.)
[8] Dingler's Polytechnisches Journal, **257**.
[9] Centralblatt f. Accumulatoren und Elementen Kunde, **11**, 73, 173. quoted by Fèry.
[10] Bull. Soc. Chem. (1903), **29**, 151, and (1904), **31**, 239.

In order to decide between the latter alternatives, two samples of electrochemically prepared oxides were analyzed for "active oxygen" and for lead. Sample No. 1 was obtained on a platinum anode from a lead nitrate solution. In preparing Sample No. 2 a small grid of antimony lead was made and filled with a paste of litharge and sulphuric acid, which was then given a prolonged charge. From this grid pellets of active material could be readily removed for analysis.

The "active oxygen" in the oxides was determined by the method of Lux as modified by Chwala and Colle.[11] A portion of the oxide was placed in a flask, an excess of standard oxalic acid added, then dilute nitric acid. The mixture was boiled until the oxide dissolved, after which the remaining oxalic acid was titrated with standard potassium permanganate. The lead in the solution was then precipitated by sulphuric acid and the resulting lead sulphate weighed. The results of these determinations are given in Table II.

TABLE II.

Sample	Weights					
	$PbSO_4$	Pb	PbO	Active Oxygen	PbO + Active Oxygen	Ratio Pb/PbO_x
1	0.8489	0.5799	0.6247	0.04587	0.6706	0.8648
1	0.7738	0.5285	0.5694	0.04260	0.6120	0.8636
2	0.5004	0.3418	0.3682	0.02625	0.3948	0.8660
2	0.6590	0.4502	0.4850	0.03408	0.5191	0.8670
2	0.7870	0.5376	0.5792	0.04178	0.6210	0.8658

Since 0.866 is the ratio of the atomic and molecular weights of Pb and PbO_2, Table II shows that the material deposited on a platinum anode and the active substance of a positive plate are chemically identical, and well within the experimental error, of the composition PbO_2. The three determinations on Sample 2 (accumulator active material) were made after the plate was charged 2, 3, and 5 days respectively, to see whether higher oxides are produced upon prolonged electrolysis, with, however, negative results. The lower factor for the content of lead obtained by Hollard by using the weight of the dried deposit is evidently

[11] Z. anal. Chem., **50**, 209.

due to persistent hydration. Fèry found evidence of higher oxides than PbO_2 in the material of a positive plate by determination of the "active oxygen," a result which the above determinations have completely failed to confirm.

As far as we can determine, no lead oxides higher than PbO_2 have been reported in chemical literature. Indeed, no element in the fourth group of the periodic system has ever been shown to have a valence greater than four. That lead peroxide forms hydrates, *e.g.*, H_2PbO_3, is, however, well known.

In the light of these results it became of interest to examine Fèry's statement that lead peroxide will not produce as high a potential, against a reference electrode, as will the active material of a positive accumulator plate. According to his experiments, material from a positive plate when placed in contact with a platinum sheet gave 2.5 volts against a zinc electrode, whereas chemically prepared PbO_2 invariably gave 0.7 volt. Here again we have failed to confirm his work. In our experiments oxides from different sources were placed in electrode vessels containing sulphuric acid and coils of platinum wire. These electrodes were connected with calomel electrodes in N/10 KCl. This involved a liquid junction, but it had, obviously, the same value in each case. The potentials were measured at room temperature with a potentiometer. Table III gives the potentials obtained, each figure being the average of twelve measurements made during the course of a week. The variations were of the order of a few millivolts.

TABLE III.

Measurements of Cells: Pt, PbO_2, H_2SO_4, KCl (N/10), HgCl, Hg.

Source of PbO_2	Potential
Active material from accumulator	1.300
Anodic deposit on platinum	1.299
Chemically prepared oxide	1.308

These results confirm those of Streintz[12] and of Strecker,[13] who both found that an electrode formed from chemically prepared PbO_2 will reach the same potential as a positive accumulator plate. If a spiral of lead wire were substituted for the

[12] Wied. Ann. (1889), 38, 344.
[13] Electrotech. Z. (1891), 435, 513, 524.

platinum used in the above experiments, a much lower potential was obtained. However, if the active material is formed electrochemically on the surface of the lead, the potential obtained agreed closely with the figures given in Table III.

4. DISCUSSION.

Since the results in Section 3 go a long way toward confirming the "double sulphate" theory of Gladstone and Tribe, there remains the problem of reconciling these conclusions with the small amount of acid reacted upon per Faraday of current, *i. e.*, with the low values of ϕ, as found in the experiments described in Section 2. Possible explanations of this anomaly are (*a*) the formation on the positive plate of mixtures of $PbSO_4$, with intermediate oxides such as Pb_3O_4, (*b*) the formation of mixtures of PbO and $PbSO_4$, and (*c*) the production of basic compounds such as $(PbO)_x(PbSO_4)_y$. Although the formation of oxides and basic compounds in the presence of strong acid may seem strange at first sight, it must be recalled that the electrode reaction involves the consumption of sulphate ions, the formation of water, and also, the passage of the current is due to a large extent to the movement of the sulphate ions a w a y from the active material. It is probable, then, that the pores of the positive plates may contain very dilute acid during discharge. Further work on this subject is now in progress.

Cambridge, Mass., and Urbàna, Ill.

DISCUSSION.

W. D. BANCROFT[1]: It is certainly very important that we should know what the real reaction is in the case of the lead storage battery, and we hope that at some subsequent meeting Mr. MacInnes will give us the rest of the information.

L. D. SIMPKINS[2]: I want to ask if you ever found an accumulator on the market where the PbO_2 on the plate ran 100 percent

[1] Professor of Physical Chemistry, Cornell University.
[2] Research Laboratory, National Lead Co., Brooklyn, N. Y.

pure? I believe it is impossible to get such, and perhaps this might have something to do with the 1.50. Also, were there any other salts present in the paste that might affect the 1.50?

D. A. MACINNES: It is general practice not to charge commercial plates completely in order to leave a frame or network of lead sulphate to support the more friable active material. Unless this framework takes part in the reaction, I don't see how it would affect our conclusions. Further, our results show that a plate made from a lead oxide and sulphuric acid paste, if charged long enough, will give 100 percent PbO_2.

L. D. SIMPKINS (*Communicated*): The authors of this paper are basing all their results from variation in density of sulphuric acid before and after discharge. These variations are very small, that is, differences do not show before the second decimal place. These small changes might occur for other reasons, namely, persulphuric acid is quite frequently formed, as pointed out by Elbs & Schönherr. Also if you take some KI and add it to the acid before and after discharging, you will find I to be liberated after charging, showing presence of other constituents.

Furthermore, the authors claim that Pb_3O_4 might be found, which would explain the apparent anomaly. As a matter of fact, Pb_3O_4 can't exist in presence of H_2SO_4, as PbO_2 and $PbSO_4$ would result.

Also there remains the fact that no commercial accumulator runs 100 percent PbO_2 on the plate.

CH. FERY[1] (*Communicated*): The authors have found that PbO_2 and peroxide of the positive plates of the accumulator gave 1.3 volts with a calomel electrode.

The measurements were made with a potentiometer.

The explanation of this result, which seems to disagree with my experiments, is very simple. During the adjustment of the potentiometer the current may be sent into the element under observation in one direction or the other, the current becoming zero only at the moment of adjustment.

It is to be feared, using this method, that the compound PbO_2 received oxygen arising from the current of the potentiometer.

[1] Laboratoire D'optique, École Municipale de Physique et de Chimie Industrielles, Paris, France.

In this case a trace of a higher oxide than PbO_2, perhaps Pb_2O_5, would give the voltage of that compound. I never was able to obtain a continuous discharge from the Zn-PbO_2 element above 0.7 volt.

On the contrary, the positive material of the accumulators gives with the Zn a discharge of 2.4 volts, which is followed by a secondary discharge of 0.7 volt.

The first corresponds to the change of Pb_2O_5 to PbO_2 and the other discharge to the reduction of the PbO_2.

Besides, the other chemical and physical properties which these two oxides possess are distinctly different.

	Pb_2O_5	PbO_2
Color	Black	Chestnut Color
Effect of Hydrogen....	Reduction under evolution of heat and change of color	No reduction in the cold state
Resistivity.....	1	22
E. M. F. with Zn.....	2.4 volts	0.7 volt

I should like to see the authors of this paper make comparative tests of the discharge of the chemical PbO_2-Zn cell and electrolytic peroxide-Zn cell. They will find that the first element will give one stage of 0.7 to 0.5 volt, while the second element shows two stages, the first from 2.4 to 0.7 volts, and the other from 0.7 to 0.5 volt.

D. A. MACINNES (*Communicated May* 25, 1920): Since reading Professor Fery's discussion, we have measured, with a voltmeter, several cells of the form Zn, H_2SO_4, PbO_2, Pt. The peroxide samples included two different commercial preparations and a freshly prepared sample made by oxidizing sodium plumbate with bromine. The oxides were placed in contact with platinum electrodes in porous cups. In each case the potentials were the same: 2.4 volts. Charging of the material by an unbalanced potentiometer was, obviously, impossible in this case.

We have made every effort to find a higher oxide than PbO_2, since the presence of such a compound would give the readiest explanation of the low consumption of acid during discharge. We have, however, found no evidence whatever of its existence.

D. A. MACINNES (*Communicated November* 6, 1920): In regard to Mr. Simpkins' communication, I can not see that "all our results" are based on variation of density of sulphuric acid. The variations of ϕ from 2 hardly admits of question since the density determinations were accurate to a few thousandths of a percent, and were of a much higher accuracy than the reproducibility of the phenomena called for. Further, as the paper states, the results agree with the earlier workers with the exception of Kohlrausch and Heim, who give almost no details of their experiments. The early work of Schenk and Farbaky and of Pfaff has been ignored, and that of Kohlrausch and Heim quoted frequently, since the latter agrees with the conceptions of Dolezalk, who, apparently, constituted himself a special attorney for the unmodified "double sulphate" theory.

In regard to persulphates and other soluble oxidizers, we have tried the reaction with KI on a charged and partly discharged cell and also on the original acid from which the electrolyte was made. No large differences were perceptible, certainly not enough to account for large variations in acid density. However, at high current densities, persulphates, etc., may possibly form. We will follow this interesting suggestion further.

Lead oxides and basic sulphates could not exist in the presence of sulphuric acid unless, in the depths of the pores of the plate, the acid is very weak, or more probably, the oxides or basic sulphates are protected by a film of lead sulphate. We are investigating this question at the present time.

A paper presented at a meeting of the New York Section of the American Electrochemical Society, and called up for discussion at the Thirty-seventh General Meeting of the Society, in Boston, April 8, 1920, President Bancroft in the Chair.

A NEW CYANIDE.[1]

By W. S. Landis.[2]

Some thirty years ago the new use of cyanide in the gold industry brought to the attention of the chemical world the necessity of producing this material on a larger scale than had been previously done, and at the same time of finding cheaper methods of preparation if the compound was to find an extended use. American, French, English and German chemists attacked the problem most energetically and from their work arose the present-day processes, with which, as far as they have become commercially practicable, you are probably familiar.

Two German chemists, working on the barium carbonate process some twenty years ago, attempted to supplant the expensive barium salt with a cheaper calcium salt and obtained a new product, cyanamid, which afterwards formed the basis of development of the well-known "cyanamid process." To a certain extent they were disappointed at the outcome of their work as the new product calcium cyanamid had little in common with the object of their search and after its discovery they sought for many years to convert cyanamid into cyanide. Their first patents on this transformation of cyanamid into cyanide were taken out eighteen years ago, these patents covering a process of fusing crude cyanamid with common salt in the proportions preferably of one part of cyanamid to two parts of sodium chloride. The mixture of cyanamid and suitable chloride was to be heated to fusion and until foaming of the mass ceased, which operation was reported to require from one-half to one hour. The resulting product was reported to contain cyanide of calcium but no analyses were given.

In attempting to carry out this process on a commercial scale, apparently they met with a great deal of difficulty. I visited their

[1] Manuscript received January 26, 1920.

[2] American Cyanamid Co., New York City.

plant in 1914 and found a great many types of equipment had been installed at one time or another, none of which had worked successfully, and the cyanide plant had been closed down and abandoned for some years.

The earliest type of apparatus consisted of a row of iron crucibles set in a gas-fired furnace with the top flush with the roof of the furnace. These crucibles were about 48 inches (122 cm.) deep and 20 inches (51 cm.) in diameter and had been made at various times of cast iron, cast steel and welded soft steels. In operation salt was melted in the pot and cyanamid was then stirred in and the whole mass kept fused for a suitable length of time. The transformation efficiencies were extremely low but no actual record of the same was made public.

The next development consisted in setting two iron crucibles side by side in the furnace. In the one crucible they charged salt and melted it, and in the second they charged cyanamid and heated the same to redness. Molten salt was ladled from the first crucible to the second crucible and when a proper quantity had been added the whole mass was kept melted until by chemical analysis the maximum yield of cyanide had been attained. The contents of the pot were then ladled out and cast into slabs.

The enormous amount of hand labor involved in this operation rendered it commercially impracticable and a new equipment replaced the old. A revolving furnace was constructed with an enlarged melting hearth midway between the tires. Salt was melted in this hearth and tapped into an iron ladle and conveyed to a crucible containing red-hot cyanamid. This operation was also unsuccessful in that there was very considerable wear and tear on the salt melting furnace and further great care had to be exercised in pouring the molten salt onto the heated cyanamid as the initial reaction was very violent and the pot frequently boiled over.

The maintenance of the externally heated crucible at the required high temperature became quite burdensome and a new type of furnace was developed in which an iron pot, provided with a spout, was set into a fuel-fired furnace. This pot was built of welded flange steel. It was 3 feet (0.92 m.) deep and 2½ feet (0.76 m.) in diameter. There was also provided an electrode 5 inches (12.7 cm.) square and hung on a chain block in line with

the axis of the pot so that it could be lowered into the fused mass contained in the same. In this way a single-phase furnace using about 40 volts and 1,200 amperes was made in a setting also provided for initial fuel firing. In operating cyanamid was charged into the bottom of the pot and heated to redness by the fire underneath. Salt was melted in the rotating furnace above described and was slowly poured into the electric furnace at such rate that no very violent reaction ensued. The carbon electrode was then lowered, the current turned on, and the whole mass kept heated electrically until the reaction was complete. The cyanide was tapped through the spout and cast into slabs.

This furnace and process was not successful—the efficiency of nitrogen transformation was very low and the final product contained a comparatively small percentage of cyanide. I was informed, however, that the same type of furnace was successfully being used in another part of Germany, where the salt was melted electrically and there was being turned out in this second plant a grade of product containing 40 percent equivalent potassium cyanide at an efficiency of nitrogen transformation of over 90 percent. I accordingly visited this other plant and was very much surprised to find there an entirely different type of apparatus in use.

At this second place I found they had tried the combined fuel-fired and electric furnace just described, and had come to the conclusion that the uneven distribution of electric energy throughout the bath caused very uneven heating of its contents, and which was believed to be the cause of the very poor efficiency obtained from the process. The iron pot would last only two or three runs before cracking and they had abandoned this type of apparatus for a resistance type of electric furnace built of brick. This improved furnace was of the tilting type with a rectangular hearth and arch roof and lined with magnesite brick. The side walls were formed of carbon blocks and electrically connected with a source of current. In practice these blocks were short-circuited with a rod of carbon, and salt was thrown into the furnace and melted around the rod, thus establishing a path of current between the side electrodes. The furnace was then filled with salt. Cyanamid was then added to the melted bath and the heating continued until by chemical analyses the maximum content of

cyanide had been formed, when the molten bath was poured out and cast into slabs. I witnessed several operations of this furnace and found that the furnace produced about 400 kilograms of molten product in from three to four hours. The apparatus used about 21 volts and 2,800 amperes. The equivalent potassium cyanide in the final product ran from 8½ to 17½ percent in the various runs and the nitrogen transformation efficiency from 40 to 75 percent. During the last run I witnessed, the furnace became blocked with a white spongy material and all operations were abandoned.

It is thus apparent that in the fifteen years elapsing between the initial experiment and my visit the Germans had been able to do little or nothing with the process of transforming cyanamid into cyanide. They had tried out many types of furnaces none of which were successful in any marked degree and had produced only a small amount of product of comparatively low grade and at great inefficiency. They were firmly convinced that it would be necessary to use more than two parts of salt to one part of cyanamid in order to make reaction take place at all and that for smooth working at least three parts of salt to one of cyanamid was absolutely necessary, also premixing of the charge was wrong chemically and must not be used. On the basis of these mixtures the final product should test between 15 and 20 percent of equivalent potassium cyanide. There were many theories and ideas advanced on the subject but I could find no comprehensive chemical study of the process and little information of scientific value. In fact the outlook for this transformation was most discouraging.

In the late fall of 1916 there was a sharp advance in the price of cyanide in this country and a great shortage in the available supply. The gold and silver mills of the continent faced a serious situation and finally one of the large users of the material came to the American Cyanamid Company with a request that it endeavor to co-operate in producing the necessary requirements of this material. With the discouraging report on the German process in hand and no time available for experimental work, the outlook was not particularly bright, but the problem was attacked and a plant was designed and equipped using resistance furnaces of a modified design, and the older German procedure was altered

somewhat with the hopes of obtaining at least results as good as the Germans had anticipated.

This plant was put into operation at Niagara Falls late in December, 1916. It was provided with five resistance furnaces of a tilting type and two salt melting furnaces of fixed type. While completing the salt melting furnaces, the resistance furnaces were put into operation as combined salt melting and reaction units. They were very much larger than the German furnaces and the design and construction was quite new. They functioned extremely well as such furnaces go, considering the complicated operation. The time of an operation, including salt melting and reaction, was reduced to about 2½ hours and the salt melting furnaces were never used for their intended purpose.

Salt, charged cold, was first melted in the furnace by adding directly to the hot furnace, the heated walls conducting sufficient current to start the melting. Into this bath of molten salt cyanamid was fed by hand, stirring up the bath with an iron rod, and as soon as all the cyanamid was in, the furnace was tapped by pouring into chill cars. After cooling, the cake was broken up and loaded into caustic soda drums which formed the shipping container of the final product. Later it was tapped directly into the shipping drums.

The process was somewhat troublesome to carry out. The life of the low-grade magnesite brick lining, the only kind then obtainable, was at most six weeks. It then became so conducting, due to the iron content of the bricks being reduced by the cyanide and through its absorption of the cyanide itself, that relining was necessary. Further, the addition of the cyanamid had to be slow and cautious as considerable foaming took place during the reaction and the contents of the furnaces would frequently boil over. The first great improvement was the discovery that the addition of a very small amount of calcium carbide to the furnace would entirely stop the foaming. This permitted the cyanamid addition to be made very quickly and the power input was, therefore, increased to obtain the additional melting speed. I had learned in Germany that the furnace men over there were of the very fixed opinion that at no time should the temperature of the bath rise above 960° C. or decomposition of cyanide would result. Due to an accident to the electrical system at Niagara one of the furnaces

received an undue amount of electrical power in one of the runs and the temperature shot up several hundred degrees above the limit set by the Germans, yet most excellent results were obtained. All furnaces were, therefore, operated at the highest possible temperature and as a result within three months of the starting of the plant the Cyanamid Company not only maintained a daily production rate of nearly four tons of sodium cyanide but had carried on experimental work which had enabled it to dispense entirely with the salt melting furnace, as well as some of the reaction furnaces, to cut down the time of reaction to half, to avoid foaming, and further to increase the test of the finished material up to approximately 24 percent equivalent sodium cyanide.

The unsatisfactory performance of the tilting furnace led the Cyanamid Company to experiment with a new type using a suspended electrode and the combination arc-resistance method of heating. The success following this development enabled it to abandon the numerous small resistance furnaces and concentrate its efforts in a single unit and at the same time obtain a very greatly improved product. After a short period of development there was constructed at Niagara a single-phase furnace with conducting hearth and containing a single suspended electrode and which furnace starting with an initial capacity of some 10 to 12 tons of product per day running about 28 percent sodium cyanide equivalent, is now operating at nearly 30 tons of product per day averaging 42 percent equivalent sodium cyanide. Additional furnaces are in process of construction.

The development of the industry has been quite rapid. In 1917 there was produced approximately 2,187,000 pounds equivalent of 100 percent sodium cyanide. In 1918 this grew to 2,350,000. In 1919 a very considerable revision of the process and equipment was made and as a consequence the plant operated only seven months, during which period it produced at the rate of over four million pounds of NaCN per year. The quality of the product started at about 14 percent equivalent sodium cyanide in January, 1917, and in August, 1919, ran uniformly between 36 and 37 percent equivalent sodium cyanide. Material running as high as 50 percent equivalent sodium cyanide has been produced and there have been shipped several carloads running around 45 percent, of which I shall speak more later.

The process and apparatus used for manufacturing this product has been extensively described in the many United States and foreign patents covering the process. Essentially cyanamid, salt and calcium carbide are mixed together and continuously fed to a single-phase furnace designed so that it has a very small cubical capacity as compared with the power input. Melting is extremely rapid and the fused product is removed from the furnace almost continuously to a cooling device which instantly chills the product. This is necessary to prevent reversion of the initial reaction, whereby calcium cyanamid, plus its contained carbon, is converted into cyanide. The proportions of cyanamid and salt vary with the product to be made.

In 1917 operations were started with two parts of salt to one part of lime nitrogen and gradually decreased in salt content until in making the present standard 42 percent product more cyanamid than salt is being used. The large furnace has been successfully operated with proportions as low as two parts of cyanamid to somewhat less than one part of salt, and the experimental furnace with no salt whatever.

The resulting product is marketed in the form of small, thin scales of a grayish black to shiny black appearance and the standard grade, known as Aero Brand Cyanide "Grade X" contains between 36 and 37 percent equivalent sodium cyanide. This method of expressing its composition is used because it is sold on the basis "per pound of sodium cyanide equivalent." A constitutional analysis of the material has so far proven impossible of execution, but evidence points to the fact that it consists of a mixture of calcium cyanide, sodium chloride and free lime with fractions of a percent each of calcium carbide, calcium cyanamid, and other minor impurities obtained from the ash of the coke used in cyanamid manufacture. The product known as Aero Brand Cyanide "Grade XX" contains about 45 percent equivalent sodium cyanide,—the cyanogen being actually present as calcium cyanide,—a slightly higher percentage of free lime and a materially lower percentage of salt than the X grade.

As to the use of this material it has found an enthusiastic reception in the mining industry. Being made from cyanamid, one of the cheapest forms of combined nitrogen, and common salt, its cost of manufacture and its selling price are materially less

than the purer forms of cyanide hitherto on the market. The use of caustic soda drums for packing has cut down the expensive item of metal containers forced upon the early industry.

The first Aero Brand cyanide made in 1917 went into the precious metal industry after a short series of laboratory tests in which it was demonstrated that it would dissolve gold and silver with equal efficiency to the 98 percent grade then in the market, and that the accumulation of soluble salts due to the cyclical use of solutions in the mill would not prove troublesome. In mill scale operations the drums were opened up and the cyanide placed in a revolving tumbler which dissolved it in water, thus giving an opportunity for any acetylene produced to be evolved outside of the mill solutions. Containing as it does a small amount of insoluble material, part of which is carbon, difficulty with precipitation due to the presence of this carbonaceous material was feared, and the solutions were therefore filtered before passing into the mill circuit. Experimental work quickly determined that the carbonaceous residue had no precipitation effect upon cyanide solutions of the precious metals and this early practice of presolution was quickly abandoned and from thence to the present time Aero Brand cyanide is dumped directly into the mill circuit.

The presence of a small amount of sulphur in the cyanamid is carried through into the Aero Brand cyanide as a sulphide. Difficulty was feared with the presence of this sulphide, but several years' experience has shown that the aeration as employed in the cyanide mills quickly oxidizes these sulphur compounds and renders them harmless. As a result no trouble has been experienced from its sulphur content.

In the gold industry, where the cyanide consumption per ton of ore is comparatively small, no difficulty has ever been experienced with the accumulation of soluble salts. In the silver industry, where cyanide consumptions of not over five pounds equivalent potassium cyanide per ton of ore is experienced, they have similarly had no trouble from accumulation of the soluble salts, but where consumptions are considerably above that figure, certain difficulties have made themselves shown in several of the silver mills. The calcium chloride obtained from double decomposition of calcium cyanide and sodium chloride acts as a precipitating agent and greatly assists in the settling of the mill solutions. Its

accumulation in such a solution, however, to an undue extent, particularly in the case where cyanide consumptions run from 10 to 100 pounds per ton of ore or concentrates leads to a decrease in the available alkalinity of solutions, and steps have had to be taken to eliminate it. These steps consist in the addition of any simple precipitating agent for lime, the precipitated lime being removed in the filter with the mill tailings.

In every case, either in the laboratory or in the mill, the cyanogen content of Aero Brand cyanide has proven itself equally as efficient in the extraction of precious metals as that of the 98 per-cent sodium cyanide pound for pound of contained cyanogen, added to which are the advantages of a considerably lower cost, slight alkalinity of the Aero Brand cyanide, and the marked influence on the rate of settlement of the solution. The new product has found a most favorable reception in the industry and is very widely and extensively used today. In the gold mills it offers no problem in handling and causes no difference in the practice beyond the fact that the making up of a stock solution is not considered as good practice as the dumping of the cyanide directly into the barren solution along with the ore. In the silver mills, using a considerable quantity of cyanide per ton of ore, simple precipitating methods for eliminating accumulated lime are in use, otherwise their practice is in no way affected.

In its present state of development Aero Brand cyanide is not adapted to use in the case hardening industry or in electroplating. For the case hardening industry it is very questionable if it has anything to offer in the future, but in the electroplating industry steps are being taken to perfect a method to simply convert it into forms such as the electro-plater can conveniently use, and it will undoubtedly make some headway in that industry.

For the preparation of cyanides it is a simple matter to dissolve Aero Brand in water, adding sufficient soda ash to eliminate the lime and filter. It is then ready for precipitation of the various insoluble cyanides.

For the preparation of ferro-cyanide it is very satisfactory. A solution of ferrous sulphate is made up of suitable strength and into this is dumped an equivalent amount of Aero Brand cyanide and the mass agitated for a short time. Quantitative transformation of the cyanogen in Aero Brand to ferro-cyanide readily

takes place. The insoluble material left in the treatment vat is filtered off, the filtering operation not being very complicated, but the amount of cake to be handled is considerable. The resulting ferro-cyanide is then concentrated and at a certain density about 95 percent of it will separate out as a meal and the other 5 percent will remain behind in solution with the chlorides of calcium and of sodium. The meal is separated in a salt filter attached to the evaporator and the solution is thrown away. Recrystallization of the meal with return of mother liquor to the original treatment tank yields a sodium ferro-cyanide of remarkable purity. The transformation can be accomplished with not over 5 percent loss of cyanide.

Recently the manufacture of anhydrous prussic acid from the crude cyanide has been successfully undertaken. Into an acid-proof generator Aero Brand cyanide and water is charged, the apparatus closed up and sulphuric acid run in. A considerable evolution of prussic acid gas takes place and the solution in the generator is finally cleared of all prussic acid by the admission of live steam. A brine cooled condensor liquefies the gas evolved from the still and condenses an impure acid containing about 80 percent prussic acid. This is charged into an iron still and re-evaporated, the resulting condensate being about 98 percent pure, in which state it is used in fumigating in the citrus growing districts. The resulting liquefied product is water white and practically chemically pure, at most containing only the most minute traces of foreign products. The construction and operation of the liquid gas plant, as the same is called locally, has been a most successful operation in every way, the only regret being that the installation was not about three times as large as originally planned because of the great demand for the high quality material it has turned out.

There is no reason to doubt that Aero Brand cyanide will find a place in many other chemical industries as up to the present time practically no limitations in its use have been found and no chemical properties which prevent its utilization in the many cyanide derivatives. Quite recent developments have shown the feasibility of manufacturing the higher-grade product containing above 45 percent equivalent sodium cyanide. These developments are too new to present at this time. A discussion of the pro-

cess or of the use of the resulting product, which has several new characteristics will be reserved for the future.

Conclusions.

The development of the process of transforming cyanamid into cyanide marks another triumph of the American electrochemist. We accomplished more in a few months than the foreign chemists accomplished in fifteen years. Three months after starting the designs of a plant our American chemists were producing to the extent of four tons of equivalent sodium cyanide per day of a much higher grade than the Germans had ever hoped for. Within a year we had reduced our operation to a single small electric furnace of a continuous type and produced a product of higher cyanide content than the Germans ever thought possible and at a nitrogen efficiency of over 90 percent.

The resulting product of uniform quality and excellent physical characteristics has found a very increasing market in the various industries using such a product and is today pushing the pure high-grade product steadily out of its long entrenched fields. For the present year the outlook is for a consumption of Aero Brand cyanide equivalent to nearly 5,000 tons of 100 percent sodium cyanide. With further development along the lines of transforming this material into its many other derivatives, particularly in view of the very low cost of the raw materials entering into its manufacture, and the simple apparatus and process used, we confidently look forward to cyanide made from cyanamid dominating the world's cvanide market.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

ARC IMAGES IN CHEMICAL ANALYSIS.[1]

By Wm. Roy Mott.[2]

Outline.

I. Introduction.

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- Colors and Position of Deposits on Upper Carbon,
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IV. Means of Separation—
- Distillation Position.
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I. INTRODUCTION.

The new arc image method of chemical analysis depends upon observing with a magnified arc image the changes of color of the arc parts in combination with other arc phenomena and especially the nature and position of the deposits on the upper and lower carbons as the materials are fractionally distilled by the arc. In going from mercury boiling at 357.2° C. to tungsten boiling at 6000° C. there is a very great range of temperature for distillation separations. In addition, unique identifying arc effects can easily be found for any element.

The new methods of analysis, using the arc images, are simple, quick, delicate, automatic, semi-quantitative and comprehensive. Good tests are given later for sixty-five elements. Any of these can be quickly and easily identified in a few minutes in their ores, alloys, oxy-compounds or in small, very impure samples. The chief impurities are usually automatically discovered as the distillation proceeds. In mixtures of three metallic compounds—especially oxy-compounds—complete identification should be obtained in less than a quarter of an hour. The tests, so far developed, will identify on the average nine out of ten in unknown mixtures of any ten of these sixty-five elements. Very delicate tests (sensitive to 0.1 mg.) apply mostly to the uncommon, valuable, and refractory elements, which take so much time and skill to identify by the usual wet methods. In regard to halogen salts, the best procedure is to form oxy-compounds by alkali carbonate fusion, or other means. The tests as given apply directly to all ores, minerals, refractories, oxides, oxy-compounds, carbides, metals and alloys.

Future developments should lead to an extensive use of arc image analysis, as it supplements and aids all other means of analysis. It is much like a refined blow-pipe analysis in utilizing colored beads and deposits. It is like fire-assay in using metal bead separations. It is like spectrum analysis in using colored light. Finally, it is like micro-chemistry in utilizing magnified phenomena. These similarities explain its comprehensiveness and indicate a large field for further study.

Checks on unknowns are quickly made by adding a little of the element being tested for and then carefully comparing the results.

Simultaneous use of two arc images on the same screen offers interesting possibilities.

II. APPARATUS.

The essential apparatus, Fig. 1, consists of a carbon-arc lamp (preferably in a hood) arranged to project a magnified arc image into a dark room.[3] Usually a magnification of twenty diameters is used, but for a few very dim arcs small arc images develop the colors better by employing a screen quite near the lamp

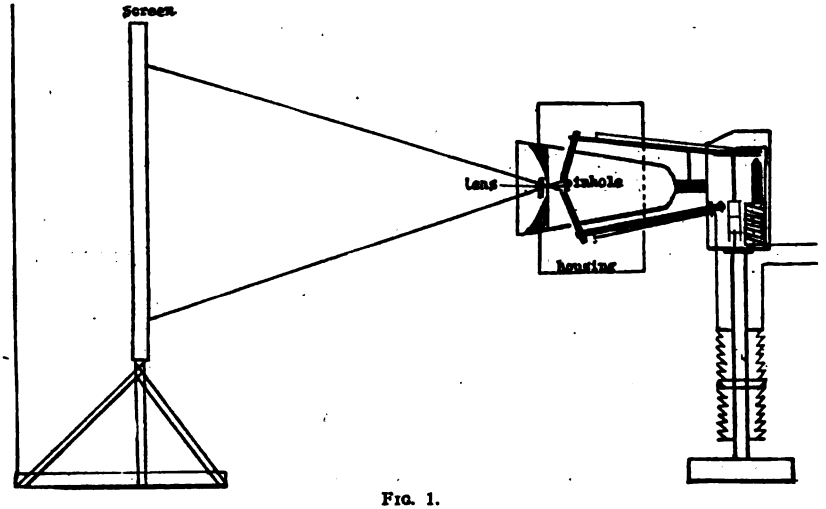

FIG. 1.

(8 inches, 20 cm.). The lamp is trimmed with carbons from a standard solid carbon cut in two (½ x 12 in., 13 x 305 mm.) such as are widely used in enclosed arc lamps. In one end of the lower carbon, hereafter called the cup, is drilled a depression ⅜ in. (10 mm.) in depth and in diameter, rounded at the bottom. An average test sample should weigh about 0.5 gram. With smaller weights of material, a shallower cup saves time.

The lamp is arranged to operate automatically at 25 amperes and 50 (arc) volts from a 110 volt D. C. line, with lower cup positive unless otherwise stated.

[3] See Trans. Amer. Electrochemical Society (1917), 31, 365.

III. MEANS OF IDENTIFICATION.

The resources for arc analysis are arc image phenomena, flame tip color, sparks, smoke, odor, sequence of distillation, and especially the nature and color of the deposits on the electrodes. The modification of these phenomena by added reagents is extremely significant.

Among the arc image phenomena, especially significant are the character, size, and brightness of the positive and negative craters, and the colors of the arc parts, both crosswise and lengthwise of the arc. A special vapor luminescence near the positive crater is characteristic of some materials, for instance red is unique to calcium oxide. The arc length and number of arc breaks are less valuable, although suggestive of class position. Short intermittent flaming arcs are characteristic of materials less volatile than carbon.

Many phenomena can be observed outside the arc image. The color of the flame tip above the arc is a very good test for sodium, lithium, boron, and copper. The kind and character of the scintillating sparks, both above the arc and on stopping it, give characteristic analytical data. A test given only by iron is the expulsion of scintillating sparks from the upper or negative carbon for several seconds after stopping the arc. The smoke from the arc is not a delicate test as a rule, but the issuance of smoke from the hot upper tip, on stopping the arc, is a very delicate, sure test for molybdenum. This effect is given by no other element. The odor helps in tests for arsenic, bromides, iodides and tungsten. A flame arc is quiet, but as the material disappears the arc changes to a noisy pure carbon arc.

The next consideration is the character of the deposit on the electrodes. The color and shape of the deposit in the lower cup is excellent for group classification. The glowing oxidation test described under tin is peculiar to the lower cup. The excellent cadmium test with the zinc oxide cloud is done in the lower cup. A few very simple chemical reaction tests in the lower cup are given for sulphur, selenium, tellurium, phosphorus and arsenic. Some beautiful colored bead tests can be obtained with silica and certain complex oxide mixes.

Among the best analytical criteria are the deposits on the side and tip of the upper electrode, as

regards color, hot and cold, and especially their position with reference to the distance inside or outside of the red and white reference rings arising from minute amounts of iron-silica in the carbons. Combinations of certain elements noted later give specially colored films upon the upper electrode of great analytical value; for instance, beautiful purples from lead and silver constitute a very delicate special test for silver.

The types of phenomena just described have been classified by elements in the latter part of the paper in such a manner that the identification of any element either alone or in complex mixtures may readily be made by an experienced observer. Identification by an inexperienced worker is possible if precaution be taken to check the observations by a blank test of the element suspected to be present.

It should be pointed out that the most striking advantages in the use of arc analysis is the rapid identification of elements or traces of elements in complex or refractory compounds where the ordinary analytical procedure is particularly difficult or tedious, and that its use in this manner does not require any high degree of expertness or practice on the part of the operator.

On the other hand, an experienced worker will find it possible to make very complex separations and identifications in mixtures of many elements. Certain of the general principles involved in the more complex separations are discussed in the following sections.

IV. MEANS OF SEPARATION

The general means of separation for complex mixtures are as follows:

1. Fractional Distillation.
2. Fractional Reduction and Separation of Metallic Beads from Oxide Melts.
3. Separation of Two Metals by Their Differing Solubility in a Third Metal Bead (*e. g.* Lead, Antimony, or Tin).

In general, a certain order of distillation is maintained. The observance of this is facilitated by replacing the upper carbon at one minute intervals during distillation. The first upper electrode will then reveal the more volatile materials, and the later ones, the less volatile materials. The tests of the latter can be improved by combining like residues from several samples. With

substances boiling from ordinary temperatures up to the boiling point of tungsten, there is a tremendous range for fractional distillation. Materials differing by 300° C. in their boiling points usually give good separations by the arc method. The iron group of metals gives the fewest separations.

The following metals or their oxides, all of which easily reduce in the carbon cup, give a definite order of distillation, beginning with the most volatile: *i. e.*, mercury, cadmium, zinc, thallium, lead, bismuth, silver, tin, germanium, copper, and gold. Then comes the iron group, chromium, vanadium, molybdenum, tantalum, and the least volatile of all—tungsten.

The refractory oxides, comprising those not reducible to metal in the carbon cup, take the following approximate order of distillation, beginning with the most volatile: potassium oxide, sodium oxide, lithium oxide, boric oxide, barium oxide, strontium oxide, silica, calcium oxide, magnesium oxide, calcium silicate, barium aluminate, alumina, titanous oxide, vanadous oxide, erbium oxide, cerium oxide, neodymium oxide, praseodymium oxide, uranous oxide, lanthanum oxide, beryllium oxide, yttrium oxide, zirconium oxide, and the least volatile of all oxides—thorium oxide.

There are certain physical principles of great importance in the control of these fractional distillations and separations in the arc.

Molten metals and oxides differ in their behavior according to their power of wetting the carbon surface of the cup. A material which does not wet the surface of the carbon forms a homogeneous molten bead in which the temperature and distillation conditions due to circulation throughout the entire mass are more constant and uniform than is the case with masses wetting the carbon, or irregular, partially molten masses. It is evident that materials spread over a considerable surface near the arc crater, will be subjected to great extremes of temperature which will seriously interfere with controlled distillation. High boiling elements will thus be volatilized from certain parts of the crater before the low boiling constituents have been completely removed from the cooler surface. This explains the reason for the use of such addition reagents as silica with the refractory oxides and of tin with the easily reduced metals. The object is to promote bead formation, or at least to obtain uniform melts, wetting the carbon,

rather than irregular partially molten masses. In general, the introduction of a third material boiling between the two to be separated gives excellent results.

For the same reason, a very deep cup gives less separation than a shallow cup owing to the unequal heating. A rotating cup should aid the separation.

Gold and all metals boiling below it form metal beads in the carbon cup. These beads do not adhere to the carbon, while all metals boiling above gold form irregular masses, wetting and dissolving carbon. With the refractory oxides the situation is just reversed. Those oxides boiling below gold (from barium oxide down) wet carbon, but those oxides boiling above gold form beads. The rare earths obey this rule in the form of oxides, but on reduction to carbide, they give masses wetting carbon. Fractional reduction and separation of metal beads from oxide melts can be accomplished by hammering, as in assaying, with mixtures of reducible oxides.

A modification of the above procedure is the use of another metal in which the reduced metal is dissolved and thus separated. We add a button of tin, removing it at regular intervals and replacing it by another. This can be repeated as often as desired. It is thus possible to secure in the successive buttons a separation of metals in the order of their reducibility under these conditions.

Separation of two metals by their differing solubility in a third metal is the third method outlined above. An example of this is the separation of gold from iron by a lead bead, in which the gold alone is soluble. Lead offers a general vehicle for separating silver, gold, palladium, platinum, and copper from the iron group of metals.

In addition to the above considerations, the addition of a third element of intermediate boiling point has certain unique advantages in arc separations by acting as a buffer between the two elements to be separated, permitting the lower boiling element to be more completely volatilized without interference from the element of highest boiling point. It is essential in this case that the intermediate element should not interfere with characteristic tests of the elements to be identified. This explains the usefulness of silica and tin as addition reagents in that they both give dim

arcs and white upper films, and so do not obscure the brightly colored arcs and colored upper films of other materials. A beautiful example of this is the use of tin to separate silver from gold. Both noble metals give green arcs making their identification difficult when distilled together. By adding tin, the green arc due to silver is followed by a dim neutral arc due to tin after which appears the green arc due to gold, thus identifying the two elements by the sequence of arc phenomena with respect to tin.

V. DISTINCTION BETWEEN SIMPLE MATERIALS AND MIXTURES.

In starting to analyze an unknown material, we first question its constitution, whether essentially simple or complex. If simple, the arc and the deposits on the successive upper carbons will be similar in character. If the mixture is complex and the boiling points of the materials are far apart, the arc changes greatly in character during the distillation. Also the earlier upper carbons show deposits of the more volatile, the later ones showing those of the less volatile constituents. On the other hand, if the boiling points of the constituents in a complex mixture are very close, the arc streams will be characterized by diffuse and poorly defined boundaries, and deposits on the upper carbons will be in general of a u n i f o r m grey or brown color without the characteristic gradations in shading which are usual with colored deposits from single elements.

VI. ANALYTICAL GROUPS.

The main system of classification, as far as practicable, is primarily dependent on the distillation order of the elements. In following this order, certain large sub-divisions, having common group characteristics, have been made. Within each group, the distillation order is strictly followed. Following the general group classification is a detailed systematic tabulation of the identifying properties and characteristics of each element. To facilitate ready reference to any element, each is numbered in the order in which it appears in this tabulation. Following the numerical classification is given an alphabetical index of the sixty-five elements and their salient arc characteristics.

Referring to the group outline, the elements have been divided into non-metals and metals. The non-metals in elemental form

do not give light and are characterized by great volatility. In general, non-metallic elements in compounds require special tests. They are less easily identified than metals. The metals can be divided into two classes:

Class *A*: Those that do not wet carbon, form molten beads, have easily reducible oxides, and give light in the core of the arc stream only.

Class *B*: Those that wet carbon when molten and give light in both the core and shell of the arc stream.

In the periodic table, Class A elements belong to the usual subgroups of easily reduced metals, while Class B elements correspond to the elements more difficult of reduction from their oxides.

It will be noted that the grouping of the elements with respect to their arc characteristics in many cases results in grouping strikingly similar to that of the periodic table. This illustrates the fundamental character of the phenomena displayed in arc analysis.

GROUP OUTLINE.

NON-METALS.

1-H, 2-F, 3-Cl, 4-Br, 5-I, 6-O, 7-S, 8-N, 9-P. The non-metals as elements do not give visible spectrum lines in the carbon arc and give short neutral carbon arcs, so that special tests are necessary.

METALS.

All have visible spectrum lines (except arsenic) and as a class increase the arc length.

CLASS A.

Metals give light in arc core only and form beads.

Group I—Metalloids, 10-Se, 11-Te, 12-As, 13-Sb are like non-metals in irregular distillation order but are like metals in giving long arcs.

Group II—Metals, 14-Hg, 15-Cd, 16-Zn, 17-Tl, 18-Pb, 19-Bi, 20-Ag, 21-Sn, 22-Ge, 23-Cu, 24-Au. These metals are arranged in their regular distillation order.

CLASS B.

Metals give light also in the arc shell. The groups I, II, and III under class B, except boron, do not leave metallic residues from the oxide compounds. The groups V, VI, and VII leave metal-like residues wetting carbon.

Group I—Alkali, 25-Cs, 26-Rb, 27-K, 28-Na, 29-Li. Decided color changes in arc stream from positive to negative.

Group II—Alkaline Earths, 30-Ba, 31-Sr, 32-Ca. Bright extraordinary band spectra with fluorides, 33-Mg, intermediate between groups II and III.

Group III—Boron Group, 34-B, 35-Si, 36-Al, 37-Be. These give a violet arc core, and an outer green shell separated by a characteristic dark space between core and shell.

Group IV—Rare Earths, 38-Er, 39-Ce, 40-Eu, 41-Nd, 42-Pr, 43-La, 44-Yt (45-Th.). These are characterized by the formation of a carbide deposit on the negative tip, which on cooling and moistening with water gives the odor of acetylene.

Group V—Iron Group, 46-Mn, 47-Co, 48-Ni, 49-Fe, 50-Cr. Unlike the previous four groups, the oxides of this group are easily reduced, giving irregular metallic residues which wet carbon and upon which is formed a dim positive crater.

Group VI—51-Ti, 52-Zr, 53-Th. The metals of this group behave like those ofGroup V, but their oxides, and especially their carbides, behave like those of Group VII.

Group VII—Elements less volatile than carbon.

Platinum metals: 54-Pd, 55-Rh, 56-Ru, 57-Pt, 58-Ir, 59-Os. These give black deposits on the sides of the upper carbon.

Ordinary metals: 60-V, 61-Ur, 62-Cb, 63-Mo, 64-Ta, 65-W. These give light-colored or white deposits on the sides of the upper carbon.

As a class, Group VII elements often give brighter craters than carbon, with rapid shifts from flaming arc to carbon arc. Marked pitting of the positive carbon is characteristic.

SPECIFIC TESTS AND PROPERTIES OF THE ELEMENTS.

(FIRST) NON-METALS.

The non-metallic elements, owing to their tightly bound electrons, are all remarkable for their volatility, poor arc conductivity, and non-luminous character in the carbon arc when considered as elements. However, compound band spectra are characteristic of many refractory oxides, alkaline earth fluorides and cyanogen. Because of their irregular distillation order, special chemical tests are given for these elements. Suitable tests were found for fluorine, sulphur and phosphorus, sensitive to small amounts in complex mixtures.

1. Hydrogen: Materials containing hydrogen (such as water, ammonium salts, organic compounds) all give very short unsteady arcs, as they are the first to volatilize.

2. Fluorine: Fluorine compounds can be quickly identified by adding calcium carbonate and observing with a small spectroscope the bright green bands peculiar only to calcium fluoride. This is a splendid test.

3. Chlorine. Chlorine compounds can be identified by adding barium carbonate and observing the green spectrum band peculiar to barium chloride.

4. Bromine: All bromides except the alkali compounds are easily detected by the odor of free bromine above the arc. With alkali bromides, tests can be made by adding to the unknown equal parts of thallium and silver nitrate which gives deposits on the upper carbon which are yellow when hot and white when cold. Chlorides give white deposits either hot or cold. Iodides give yellow deposits hot or cold.

5. Iodine: All iodides except the alkalies are easily detected by the purple iodine vapor, with its characteristic odor, above the arc. See bromine, above, for tests with alkali iodides.

6. Oxygen: As in the case of most of the non-metallic elements, a specific and universal test for oxygen is not available, although band spectra are characteristic of many oxides. It is possible, however, to very sharply differentiate between oxides and non-oxygen compounds in the case of any particular metal, as for example between titanium oxide, nitride and carbide. These

distinctions are specific for each metal. Oxides differ from halogen salts and sulphides in that the latter are not reducible to metal or carbide in a carbon cup.

7. Sulphur: Compounds of any kind are quickly and effectively tested by the blow-pipe charcoal test transferred to the carbon arc. This is done by taking 0.4 g. of sodium carbonate (sulphur free) and 0.1 g. of unknown material and heating 1 to 2 minutes with the carbon arc and then dipping in 1 to 4 hydrochloric acid solution. The hydrogen sulphide odor is noted; this test is easily sensitive to one-tenth of a milligram.

8. Nitrogen: Is not ordinarily tested for with a carbon arc. The cyanogen band spectrum in the neutral carbon arc depends on the presence of atmospheric nitrogen. Of the nitrides, boron nitride, which is the only white solid subliming above the boiling point of copper, is a striking material. The ease with which boron nitride is formed from boric oxide and nitrogen compounds suggests that this might make a satisfactory test for certain nitrogen-containing compounds.

9. Phosphorus, like boron, gives a green flame tip above the arc. This is best seen by using equal parts of strontium carbonate with the unknown. The best universal test for phosphorus is obtained by heating for 2 minutes 0.1 gram of the unknown with 0.5 gram of barium carbonate. The cup, after cooling, is dipped in water. A garlic odor is a very delicate test for phosphorus. Arsenates give a geranium-like odor under the same conditions. This test for phosphorus is very sensitive (1/10 milligram or less) except with much borate.

(SECOND) METALS.

CLASS A.

Class A metals give beads and light in arc core only. These metals, except the metalloid selenium and the subliming element arsenic, form beads in the cup. The reason for bead formation is found in their non-wetting action on carbon, owing to their inability to dissolve it. Their oxides are all easily reduced to metal, and at high temperatures are formed with very slight liberation of energy, hence no brightly colored arc shells are given. Long arcs are given by these metals, which are all far more volatile than iron, and their deposit on the upper carbon occurs

beyond the reference ring of red and white, due to minute amounts of iron and silica in the carbons. The negative craters are normal in size and no deposit takes place in them. The positive craters are relatively dim, and in some cases give curious multiple bright spots.

Group 1-A.

The metalloids, Se, Te, As and Sb, unlike the non-metallic elements, give long dim arc streams. Arsenic, like phosphorus, gives spectrum lines entirely in the ultra-violet. The metalloids distill, like the non-metals, in irregular order, depending upon the metals with which they are associated; the distillation range varies from that of cadmium to that of the iron group. Iron and similar metals easily retain some of these metalloids, including sulphur and phosphorus, up to high temperatures.

10. Selenium: Metal gives a long dim bluish-green arc stream with a red deposit on the side of the upper carbon, and is the only Class A material to wet carbon. The universal test is the use of sodium carbonate as in the case of sulphur, giving a red colloidal solution. The test is made more delicate by adding a little alkali cyanide.

11. Tellurium. The same test as described for selenium gives a dark green colloidal solution. Tellurium metal gives a good bead in the lower cup.

12. Arsenic: Unlike phosphorus, gives long arcs, with garlic odor above the arc. Like carbon, arsenic sublimes, but the arsenides form beads. When mixed with cadmium, arsenic gives a sharp white band on the upper carbon, not given by any other metal including antimony or tin. With equal parts of cadmium and arsenic, the test is delicate to a fraction of a milligram. Arsenates, like phosphates, give dim arc streams and dim positive craters. The geranium odor on fusion of arsenates with barium carbonate and dipping the melt in water, is characteristic but not recommended owing to the poisonous nature of arsenic. Copper gives a bright green deposit on the upper carbon when arsenic is added. No very delicate arc test was found for arsenic combined with metals of the iron group.

13. Antimony gives a dim bluish arc stream and a characteristic double white band on the upper carbon with less striation and less smoking than arsenic, the element most closely related to

antimony. Antimony usually distills after lead, or with copper or metals of the iron group. Antimony forms a dark bead in the cup where tin gives a white bead. The best general tests for antimony in complex mixtures are: (1) the addition of lead to antimony, giving on the sides of the upper carbon a characteristic deposit of yellow lead antimonate, and (2) the addition of copper to antimony develops a characteristic orange band on the sides of the upper carbon. These tests apply in the presence of all Class A metals, but in presence of the iron metals, the antimony should be extracted by fusion with a lead bead and the above two tests then applied.

Group II-A.

The metals of Group II of Class A have a very sharply defined distillation order. First comes the very volatile group consisting of mercury, cadmium, and zinc, and next, a group of metals similar to lead, comprising thallium, lead, and bismuth; and finally, the noble metals and tin.

14. Mercury does not give good arc image tests because of its extreme volatility. The best test is to add to the unknown equal parts of sulphur and calcium iodide, forming a yellow coat on the upper carbon, which turns red in a few hours. With this test, lead gives a yellow coat. Bismuth gives a reddish coat.

15. Cadmium gives a bluish green arc with a characteristic brown smoke which coats the upper carbon with a brown deposit. A universal, rapid and delicate test for traces of cadmium in zinc consists in heating 0.5 gr. of zinc in the cup for one-half minute. On breaking the arc a feathery growth of zinc oxide is formed in the lower cup at the tip of which appears the brown spot characteristic of cadmium. This test is delicate to 0.05 percent Cd. It can be applied to any unknown, by adding to cadmium-free zinc one-tenth of its weight of the unknown material.

16. Zinc gives a blue arc with marked smoke around the arc stream in the arc image. Metallic zinc is unique in giving in the lower cup the bushy growth of oxide described above, on breaking the arc. In a complex mixture, zinc is the only metal giving a ring around the lower electrode. This ring is yellow when hot and white when cold, except in the presence of cobalt, where it is green when cold. The same color scheme applies to the lower

edge of the upper carbon, in distinction to all other members of this group. The test may fail at less than 2 percent Zn, and hence is not very delicate. The presence of lead improves the delicacy.

17. Thallium gives an intense green arc. To separate the green arc of thallium from the green arcs of silver, copper, gold, and nickel, lead can be added. The best of all thallium tests is its spectrum green line. A thallium bead is unique in giving a long continuing dark smoke from the lower carbon after stopping the arc and in giving dark deposits on the upper carbon unlike any other metal of Class A.

18. Lead gives a very dim arc stream and is best identified by the color changes of the hot upper carbon on cooling. On the hot upper carbon there are two bands, one red (nearer the arc), and one green. On cooling, the green band turns greenish grey and the red band turns green. This furnishes a good distinction from all the other metals, but calls for over 2 percent of lead. Above the colored bands is a white deposit except in the presence of added antimony, when this deposit is yellow both hot and cold. This yellow lead antimonate is a good test for both antimony and lead. (Bismuth with antimony gives a deposit yellow when hot but white when cold). In the presence of lead, antimony or bismuth, the addition of silver forms a beautiful purple deposit on the upper carbon. If both silver and boric oxide are added to one of these metals, an intense green replaces the purple. These tests apply in complex mixtures.

19. Bismuth gives a dim blue arc stream and in the absence of lead may be recognized by the peculiar arrangement of the colored bands on the upper carbon. This consists of a wide band which is usually dull green but sometimes brown, in the middle of which is a sharply-defined band about one-half millimeter wide and usually a peculiar deep green in color. This band is always brown when hot and sometimes remains so when cold. While the colors of these bands are somewhat interchangeable, their relationship is unmistakable. Lead interferes with this test by obscuring the bands by its deposit. Like lead, bismuth with silver gives a purple upper film. Practically all ordinary bismuth contains enough silver to give this test. Addition of lead improves this purple deposit. A test applying to

bismuth in the presence of lead consists in adding boric oxide. This gives a curious and characteristic phenomenon; after distilling from one to three minutes and breaking the arc, there appears a yellow band consisting of a molten glaze under which gas bubbles are formed for a half minute or so. These usually leave a froth on freezing. To a slight extent, the same phenomenon is given by antimony and arsenic. (See mercury for iodide test.)

20. Silver gives a green arc less bright than that of thallium or copper. Silver alone gives a white metallic coat on the sides of the upper carbon. Unlike all other arc deposits, this rapidly darkens in air containing a little hydrogen sulphide. The best test for silver in any mixture is obtained by adding lead and distilling, when there forms a beautiful purple coat on the sides of the upper carbon. This test is sensitive to 1/50 milligram of silver in 0.5 g. of lead. The only other element giving a purple upper film is gold. Interference between gold and silver is prevented by the addition of tin as well as lead to the mixture. The characteristic silver arc stream and its deposits occur early in the distillation, after which appears the dim neutral arc of tin, with white deposits on the renewed uppers; this in turn is followed by the green arc stream and purple deposit due to gold and tin. If silver is mixed with higher boiling elements such as those of the iron group, the sensitiveness of the silver test may be increased by extracting the silver with a bead of molten lead which is afterwards removed and separately tested. Addition of boric oxide to the above lead-silver mixture gives a beautiful green coat on the upper carbon and an intense green smoke from the arc flame. Boric oxide is the only material giving this effect. These tests for silver are sensitive, unique, and are not interfered with by any other elements.

21. Tin gives an unusually dim, slightly greenish arc, and a bead with a white oxide coat in the lower cup following the distillation of Class A metals. Tin mixed with equal parts of lead and copper gives a molten bead which on stopping the arc rapidly oxidizes with a red glow and forms a voluminuos powdery growth of oxide which swells up in the cup. This behavior is extremely characteristic and forms a satisfactory test in the presence of all Class A metals. Tin, if mixed with elements of

the iron group, gives no satisfactory test, although it is a valuable reagent for making many delicate tests on the group metals. Tin gives on the upper carbon two white bands, the second of which is grey with copper, orange with copper and antimony, purple with gold, brown with manganese, shows a dark sharp line with nickel, is blue with cobalt and aluminum, brown with iron, and pink with chromium.

22. Germanium metal gives a very dim arc stream like that of tin, and on the upper carbon characteristic brown rings close to the negative crater. Germanium is the only metal of Class I to give a brown bead with tin.

23. Copper gives a green arc stream with a characteristic flame tip above the arc having a green inner and red outer edge. Mn and Cr are the only elements even slightly duplicating this. The upper carbon has a brown side deposit with a negative tip turning to a purplish red after about five minutes. Copper with equal parts of manganese gives a blue deposit on the sides of the upper carbon. This is a delicate test but not suited to complex mixtures. A more general test is the very characteristic orange band given by copper with antimony.

Copper can be dissolved from elements of the iron group by lead or antimony as described for silver and the usual tests are then easily made.

24. Gold, when very pure, gives a short green arc. It is the highest boiling of all elements not wetting or dissolving carbon. It comes off with tin and copper forming with tin a beautiful purple of Cassius on the upper carbon. This is a delicate test. (See silver). Gold also gives a purple upper film with zinc oxide and with many other oxides normally white. Separation from elements of the iron group by lead improves the delicacy of the purple upper film formed by tin and gold. Gold alone gives a yellow to brown upper metallic film.

CLASS B.

Metals of this class wet and dissolve carbon. Formation of a preliminary bead usually occurs, this tendency being increased by the presence of Class A metals. With continued distillation

the beads disappear, forming irregular melts wetting the carbon surfaces. Oxides of Class B metals which boil below gold, wet the carbon, but those boiling above gold tend to form oxide beads, until we reach the refractory rare earth oxides, which permit the arc to crater directly on the melt, forming the carbides, which wet carbon. Class B metals are also characterized by arc streams giving light in the shell as well as in the core (except with certain of the platinum metals).

All the elements whose oxides resist hydrogen reduction give luminous arc shells even with very minute (1/10 mg.) amounts of material; *i. e.*, groups I, II, III, IV, and VI. The easily reducible metals of Class B, groups V and VII, and of low energy intensity such as Ni and Co require larger amounts of material in the arc stream to develop luminosity in the outer shell. Less highly magnified arc images are of advantage in these cases through increased visibility of the dimmer arc shell. This is also true of the alkalies which have low energy of oxidation at very high temperatures.

Group I-B.

Alkali elements in their compounds give marked wetting action; very long dim arc streams;[4] dim, large positive craters and marked color differences in the arc stream from positive to negative. Certain very characteristic changes in the nature of the arc stream occur with the alkalies, these changes being greatly accentuated by the addition of an alkaline earth compound, especially calcium fluoride. The normal arc stream is elliptical in form, consisting in Class B materials of a core and shell in which volatilized carbon and chemical material are carried from the positive lower to the negative upper carbon. The ends of the ellipse rest upon the craters of the positive and negative electrodes respectively. In the case of the alkalies under the conditions above described there appear to be two separate arc streams from positive and negative respectively, meeting at an angle near the negative electrode. The arc stream from the positive lower possesses the characteristics of the normal arc stream with a very luminous shell, whereas the opposing arc stream from the negative upper carbon is very dim and narrow and impinges on the side of the

[4] Alkalies give long arcs with positive or negative craters on the lower cup, in contrast with Class A metals which give long arcs only with positive lower carbon cups.

large luminous arc stream from the positive, at an angle and distance depending upon the amount of alkali present. That is, as the alkali distills, the negative arc stream shortens and disappears and the positive arc stream swings over to its normal position. This is the basis of the tests given in Table I.

The alkali elements are the only ones producing this unusual arc effect. When present in large amounts, the alkalies, notably lithium and sodium, may give so high a luminescence in the arc shell that the core is obscured and the arc stream appears to be a single solid color. On continuing the distillation the relative intensity of the shell decreases and the core becomes visible. Finally, a condition is reached within which the shell is visible only at the negative end of the arc stream. The arc core is made more noticable by the materials having stronger core luminescence.

A second group characteristic of the alkalies consists in a test of their wetting power. The addition of a small percentage (2 percent) of an alkali to a material which does not wet carbon, as for example, strontium sulphate, will cause the latter to exhibit a wetting action.

TABLE I.

Duration of Initial Dim Negative Stream.

0.2 g. Mixture	Duration Dim Neg. Stream	Time to Volatilize
$\frac{1}{2}Li_2SO_4$ $\frac{1}{2}CaF_2$	10 sec.	5½ min.
$\frac{1}{2}Na_2SO_4$, $\frac{1}{2}CaF_2$	10 sec.	9 "
$\frac{1}{2}K_2SO_4$, $\frac{1}{2}CaF_2$	120 sec.	13 "
$\frac{1}{2}Rb_2SO_4$, $\frac{1}{2}CaF_2$	45 sec.	13 "
$\frac{1}{2}Cs_2SO_4$, $\frac{1}{2}CaF_2$	90 sec.	10 "

25. Caesium; 26. Rubidium; 27. Potassium: Caesium, rubidium, and potassium behave with extraordinary similarity in the carbon arc. All give very long, dim arc streams with very repellent negative arc effects and highly marked wetting power. The tests given in the following tables require previous extraction as sulphates. Table I shows the duration of the characteristic dim repellent arc stream from the negative crater in sharp contrast to the brightly flaming positive arc stream.

In Table II are given a series of good bead tests. Specified mixtures are heated in the arc cup for two minutes.

28. Sodium salts give at first a solid yellow arc stream but later a yellow arc shell, especially with mixtures. The yellow arc shell will detect 10 percent or more of sodium, using the magnified arc image, and 1 percent or more will be detected with the small arc image. One hundredth of one percent may be detected by the yellow flame tip above the arc. To distinguish the yellow sodium arc shell from other yellow shells add boric oxide, which gives the yellow sodium shell outside the green shell of boron—a combination peculiar only to sodium and applicable to complex mixtures.

TABLE II.

Alkali Colored Bead Tests with Silica and Sulphates.

$0.2K_2SO_4$, $0.1SiO_2$	Yellow irregular clear melt.
$0.2Na_2SO_4$, $0.1SiO_2$	Transparent wine red flat bead.
Above with $1\%K_2SO_4$	Appreciably flatter bead.
Above with $10\%K_2SO_4$	Brown melt wets carbon.
$0.2Na_2SO_4$, $0.2SiO_2$	Deep red hard bead, insoluble in water.
Above with $10\%Li_2SO_4$	Deeper red.
Above with $10\%K_2SO_4$	Flatter more adhering bead.
Above with $10\%Rb_2SO_4$	Light yellow bead instead of red.
Above with $10\%Cs_2SO_4$	Light yellow bead, not black when hot as with all other alkalies.

29. Lithium salts give first a solid red arc stream but later a red shell and blue core especially pronounced at the negative electrode. In mixtures a tenth of 1 percent is easily recognized. The flame tip above the arc is an intense red. Addition of potassium silicate intensifies the characteristic lithium phenomena in very complex mixtures. Lithium is the only element to give a red shell outside the green shell made by adding boric oxide. The distillation order from oxide melts is first K_2O, then Na_2O and last Li_2O followed by the alkaline earths.

Group II-B.

Alkaline Earths and Magnesium: The alkaline earth oxides distill after the alkalies in the order BaO, SrO, CaO, and then MgO, which behaves very differently from the alkaline earths. In contrast to the alkalies, which give deposits on the side of the upper carbon beyond the iron reference ring, the alkaline earths give deposits inside this ring, especially in the negative crater itself. This deposit causes the dim diffused negative craters

characteristic of this group. On breaking the arc, this negative tip deposit of carbide changes to the white oxide, which on moistening with water gives an alkaline reaction with litmus, thus affording a test peculiar to alkaline earths.

Unlike the alkalies, the alkaline earths under all conditions give sharply defined bright arc shells with bright band spectra of the oxides or fluorides. The alkaline earth fluorides are the only ones to give bright spectra except the closely related beryllium fluoride. The oxides give bright cup luminescence—green with barium, blue with strontium, and red with calcium. By cup luminescence is meant an intense glow which appears within the positive carbon cup between the oxide mass and arc crater on the carbon, which appears to be due to the oxidation of the vaporized metal at this point. This phenomenon is characteristic of the alkaline earths and of certain of the rare earths, as cerium.

30. Barium compounds give a characteristic reddish purple arc core most marked near the negative electrode and a thin green arc shell. The vanadium arc is the only one resembling that of barium. Barium gives a green cup luminescence which somewhat resembles the bluish green luminescence afforded by cerium. Barium oxy-compounds, more than those of any other element, give very large dim diffused negative craters which, unlike those of all other elements, are suppressed by adding a little alumina or beryllium oxide (because of the extremely stable barium aluminate formed). Band spectra tests with fluoride and chloride are good.

31. Strontium oxy-compounds give a blue arc core and a red arc shell, duplicated by yttrium, which differs, however, in allowing the arc to crater on the oxide melt. The blue "cup luminescence" and blue arc core form distinctions from calcium, with which the strontium distills. The universal test for strontium is the yellow spectrum band peculiar only to strontium fluoride and easily obtained on adding a fluoride to any strontium-containing material.

32. Calcium compounds give violet arc cores and bright reddish yellow arc shells. Oxy-compounds give a characteristic red "cup luminescence,"

which is increased by adding equal parts of silica. This is unique for calcium. Another unique test for calcium is given by the red and green spectrum bands developed by adding any fluoride to any calcium-containing material.

33. Magnesium oxide distills just after calcium oxide. It is like beryllium oxide (see next group III) except that the arc appears at first to be solid green, but later develops a blue-green core and a green shell, especially in mixtures. This arc is similar only to erbium. Unlike the alkaline earths, magnesium oxide does not give dim negative craters nor a deposit within the negative crater. Aluminum oxide aids in the detection of magnesium oxide in complex mixtures by preventing interference from the less volatile rare earths which follow.

Group III—B. Boron Group.

This group consists of boron, silicon, aluminum, and beryllium. These elements are close together in the periodic table. They have very stable oxides and nitrides which give short dim arcs with violet arc cores, a peculiar dark layer between core and shell and outer green arc shells (due to oxide band spectra). The oxides, as seen in the arc image, form highly insulating, transparent beads except boric oxide which like the alkalies forms a glaze on both carbons. On cooling, silica gives clear, transparent beads, alumina smooth opaque beads, and beryllium oxide rough opaque beads. Unlike the alkaline earths, these materials all give normal negative craters closely surrounded by sharp white rings. The approximate distillation order is as follows, boric oxide, silicon, aluminum, silicon carbide, boron, beryllium, boron nitride, silica, alumina, beryllium oxide, and boron carbide. The metals give long arcs but the oxides are characterized by short arcs.

34. Boron: The most delicate test for boron is the very bright green flame tip above the arc, but this is duplicated to a degree by P, Tl, Si, Mo, and Er. However, boric oxide by addition of alkali materials distills with them and is the only material to give a green inner arc shell with a yellow sodium or red lithium outer.

This is an excellent test. Boric oxide is largely volatilized with or below silver and is the only material which changes the lead-silver purple upper film to a bright green. A large number of borates give green upper films. Metallic boron distills before iron, with dim cratering and a longer arc than the oxide. Boron carbide distills after iron, giving a dim bluish spot in the otherwise bright positive crater. Boron and chromium are almost the only elements to greatly suppress the scintillating sparks of iron. Boron nitride sublimes at 3,000° C. and gives a white ring at the negative, where boron carbide gives a dark ring.

35. Silicon materials give very dim arcs and white coatings on the upper carbon. Silicon and its carbide give dim positive craters and distill the silicon before the iron. Silica has many effects but these are not very delicate for universal specific tests. The most delicate test for silica is the white ring formed at the negative tip just inside the red iron ring. This is an excellent test in the presence of materials more volatile than silica, but nearly worthless with those less volatile. In very complex mixtures, silica gives a characteristic narrow white line about 2 cm. from the tip of the upper carbon. (This effect is improved by gold). A transparent bead in the lower cup nearly always indicates silica. Distillation of complex mixtures with an excess of tin aids in forming this bead.

36. Alumina and beryllium oxide distill after all previous oxides of groups I, II, and III and both give, as a delicate test, a white ring inside the silica ring; they are the only materials which prevent barium from giving a dim diffused negative crater, and both give a blue inner arc shell with excess of tin, which is best seen with the small arc image. (This is duplicated only by lanthanum). Aluminum metal gives unique bright metal beads which squeeze out of the metallic melt on breaking the arc; an effect duplicated by no other material. Aluminum oxide gives a swelling, exploding or popping bead—especially on stopping the arc. This is prevented by adding excess of tin. Tin is an effective addition agent in differentiating aluminum and beryllium oxides (see later). A round oxide bead after distilling the silica is a good indication of alumina or beryllia in a complex mixture.

37. Beryllium oxide is the final residue from all previous oxides. Upon viewing the carbon cup in the arc image and breaking the arc, the oxide bead appears relatively brighter than the carbon cup for several seconds. This is a unique and distinguishing effect evidently due to the high specific heat and latent heat of fusion of beryllium oxide which causes it to maintain a high temperature during solidification. On solidification the clear transparent melt changes to a rough, warty bead in distinction from the smooth bead formed by alumina. By adding an excess of tin, semi-quantitative comparisons of alumina and beryllia in minerals can easily be made, especially in the presence of rare earths. Unlike aluminum fluoride, beryllium fluoride gives an arc with a yellow shell and an orange spectrum band.

Group IV-B. Rare Earth Oxides.

Rare earth oxides distill after groups I, II and III. They are unique in giving carbide deposits in the negative crater which, on cooling and wetting with water, swell and give the characteristic acetylene odor. Uranium gives a dark carbide, swelling with the addition of water but no acetylene odor. In distinction from previous oxides, the rare earths allow the arc to crater on the melt. The distillation order is: Er, Ce, Eu, Nd, Pr, La, Yt, and Th.

38. Erbium metal or oxide gives a bluish green arc core and a well defined green arc shell (see Mg). Especially characteristic is this green arc shell which comes outside of the yttrium red shell. (Erbium and yttrium always occur together). In rare earth mixtures erbium is also easily recognized by the green flame tip above the arc. The interference of the green flame tip due to boric oxide can be overcome by its distillation with the alkalies at temperatures far below those vaporizing the rare earth group.

39. Cerium gives a very bright blue arc core with an arc shell having a green inner edge which shades off to a reddish yellow outer edge. Cerium oxide gives a bluish-green "cup luminescence." Cerium, in minerals, is easily identified by the negative

tip, yellow when hot and brown when cold, due to traces of Pr or Ti always present with cerium. Pure cerium compounds give a negative tip yellow while hot and white when cold—a result duplicated by Ti and Cb.

40. Europium oxide gives an intense blue arc core and a sharply outlined, bright orange arc shell, not duplicated by the other rare earth elements here tested. The negative tip is white and gives the usual rare earth carbide reaction.

41. Neodymium gives a blue arc core with a green inner and a reddish outer arc shell. It gives a white negative tip deposit or spot. All minerals with Nd contain Pr, and tests indicating Pr also indicate Nd.

42. Praseodymium gives an arc very similar to that of neodymium. Unlike all the other rare earth elements, praseodymium alone (or with La, Yt, or Th) gives a black negative tip duplicated only by Ur. A very little praseodymium causes the cerium tip to turn dark brown when cold.

43. Lanthanum oxide gives a blue arc core, a dark inner layer between core and shell, and a yellowish green arc shell—a combination of arc shell layers produced by no other element. The best lanthanum test in complex mixtures is obtained by their volatilization with tin, observing the blue inner arc shell. The small arc image is employed here. The test is duplicated only by Al and Be oxides.

44. Yttrium oxide sharply distills after lanthanum oxide but before Zr and Th oxides. Yttrium gives a bright blue arc core and a very bright red arc shell (see Sr). This red shell offers a very delicate test for yttrium in complex mixtures. Erbium, as a persistent impurity with yttrium, gives a green arc shell outside of the yttrium red.

45. Thorium oxide distills after yttrium and zirconium oxides forming bright craters and hence is described in fuller detail in Group VI. Its carbide reaction with water is very slow compared with those of the other rare earths. In some cases small pieces of thorium carbide took half an hour to disintegrate completely in water.

Group V-B. Iron-like Metals.

Unlike the previous four groups, the oxides of this group are easily reduced to metal which allows a very dim unsteady cratering of the arc on the irregular metal melts. These melts wet and rapidly dissolve carbon. The negative craters are normal in size and brightness. These metals give colored side deposits on the upper carbon, where nearly all previous Class B groups give white side deposits. The members of this group form poorly separable mixtures giving uniformly grey or brown side deposits. However, manganese clearly distills first and chromium last. The following Table III, summarizes the arc colors and colors of side deposits.

The individual elements of this group are easily identified, but mixtures of more than three offer great difficulty. The fractional solution of members of this group by successive additions of tin and the removal of the tin beads during successive intervals of distillation, permits of delicate tests for the separate members. (See tin).

TABLE III.

Characteristics of Iron-like Metals.

Metal	Arc Core	Arc Shell	Sparks	Upper Side
Mn	Blue core	Broad yellow green	Smoke trail	Brown
Co	" "	Dim reddish yellow	Dull	Black band
Ni	" "	Dim yellow	Dull	Greenish white
Fe	" "	Bright yellow	Scintillating	Red band with yellow
Cr	" "	Green inner—yellow outer	Scintillating	Greenish white
Complex mixtures				Grey to brown

46. Manganese gives very characteristic arc streams with a very broad yellowish green arc shell which is best observed by adding tin—this also gives a characteristic brown deposit on the first upper carbon. Addition of equal parts of copper to manganese gives blue upper carbons—a characteristic test.

47. Cobalt can be easily identified in the presence of nickel, etc., by using equal parts of the cobalt-containing material, chromium and aluminum. This gives a decided blue green coat on

the sides of the upper carbon. In most cases, by the use of tin with an alumina-silica bead the characteristic cobalt blue bead may be secured. With zinc, cobalt is the only element giving a green band on the upper carbon.

48. Nickel is the only metal excepting the precious metals, to give metal beads near the negative crater. Addition of boric oxide increases this effect. Nickel alone gives a side deposit which is uniformly greenish white, hot and cold. In mixtures, tin and nickel give a characteristic black line on the upper carbon. With various silica beads, nickel gives a yellow color in distinction from cobalt blue. The nickel tests are the least satisfactory of all the tests for elements of the iron group.

49. Iron gives a very characteristic upper film having a sharply defined red band about 15 millimeters from the tip and a yellow deposit extending from this point about 10 cm. up the side of the carbon. (See Mo). Iron is the only element to give scintillating sparks from the tip of the hot upper carbon for several seconds after stopping the arc. The test is sensitive to 1 mg. of iron except in the presence of chromium or boron. Another delicate test for iron is its power to change the chromium green negative ring to a grey color at the end of the chromium distillation. With very complex mixtures, iron sufficient for distinctive tests can be dissolved out by a very hot antimony bead.

50. Chromium gives a brighter arc than iron. A peculiar arc image effect of chromium is the formation of a ring of oxide beads (2.5 cm. on an arc image of 20 diameters magnification) near the edge of the negative crater. This disappears on the cold electrode and is given by no other element. This deposit on the negative tip is black to brown when hot and green when cold (except that in the presence of iron the color when cold is grey). The best test (sensitive to 1/10 mg.) for chromium is obtained by using 0.2 gram $BaCO_3$, 0.01 gram Al_2O_3 and 0.01 gram of the chromium containing material. This gives an upper tip with a brown ring when hot and

a bright green color when cold and allows tests to be made in the presence of iron, vanadium, uranium and titanium. Uranium gives a tip deposit or spot which is brown when hot and green when cold. By changing upper carbons the chromium test may be first obtained, followed by the uranium test. Vanadium gives a blue ring and titanium with vanadium gives a brown ring on the negative electrode tip.

Group VI—B.

The metals of group VI are like those of group V but their carbides and their oxides (except Ti) follow group VII. This group consists of titanium, zirconium and thorium. As metals, these elements give dim positive craters with long steady flaming arcs, but with the formation of carbide there come intensely bright small positive craters, causing small deep pits in the lower carbon with short, unsteady arcs and dim diffused negative craters. Zirconium and thorium oxides also sustain intensely bright craters, resulting in their rapid volatilization.

51. Titanium even in minute amounts gives a bright, sharp arc stream with blue core and yellow shell having a green inner edge and a red outer edge. Much titanium oxide increases the yellow shell effect (see Na, Ca). Titanium oxide, like alumina, gives a popping bead. Titanium carbide gives the group test sharply as above described. A very delicate test for titanium in complex mixtures is an upper tip deposit, yellow when hot, and white when cold (with much titanium the tip deposit is light brown when cold.) All clays and siliceous materials easily show titanium by this test, which is only duplicated by Cb and Ce.

52. Zirconium oxide differs from all other oxides in sustaining a bright positive crater of irregular shape (with thorium oxide, the crater is nearly round). The arc has a blue core and a nearly white arc shell with a green outer shell—a combination given only by zirconium oxide and carbide. (Zirconium metal gives an arc with dim positive craters—dim blue arc core, dark layer between core and shell, and green arc shell. See Al). Zirconium gives an upper

tip deposit, white both hot and cold—a distinction from titanium. The deposit has a ring of yellow beads around it—a distinction from thorium and tantalum.

53. Thorium oxide is the least volatile of all oxides, but owing to its ability to sustain the arc crater it is rapidly volatilized when present in large amounts. Less than 10 mg. of ThO_2 does not attract the crater and hence volatilization is much slower. By making the carbon cup the negative electrode the time of volatilization is several times longer than with the other rare earth oxides under the same conditions. In distinction from Ti and Zr, Th gives acetylene by addition of water to the upper tip deposit. Thorium accentuates the yellow green deposit given by tungsten in the lower cup, which also distinguishes it from Zr. The tests common to zirconium and thorium are delicate, but their simultaneous distillation makes individual tests less delicate. The thorium arc flashes quickly and is easily obscured by zirconium. The arc of metallic thorium has a blue core with a red edge, but that of the oxide has a thick yellow-white shell with a slight red outer edge. Much thorium carbide causes an arc far shorter than a carbon arc—an effect produced by no other Class B element.

Group VII—B.

This group consists of the platinum metals and V, Ur, Cb, Mo, Ta, and W. This group contains elements less volatile than carbon and so gives short arcs in which the melt sustains the positive arc crater. With large amounts of material the craters are small and bright, and cause marked pitting of the carbon cup. With small amounts of materials, the usual crater consists of a dim bluish round pool within the brighter carbon crater. The arc stream alternates in character from that of the pure carbon arc to that of the flaming arc characteristic of these elements. The tip deposits on the upper carbons form very characteristic and delicate tests.

The platinum metals give shiny white metal in the lower cup and upper tip (resembling Ni and Ag) and give dark or black deposits on the sides of the upper carbon, especially when mixed with rare earths. Dark or black upper carbon side deposits are also given by carbon

from organic materials; thallium and cobalt give black bands on the upper carbons. The distillation order is Pd, Rh, Ru, Pt, Ir and Os.

54. Palladium is the most volatile. It gives a bright green steady arc with no arc shell, resembling silver. Palladium is separated from silver by addition of iron and distilling. Palladium gives a dark brown deposit on the side of the upper carbon—a distinction from other platinum metals. With a complex mixture, palladium can be readily dissolved out by a lead bead and tested as above.

55. Rhodium gives a bluish-green arc core with a dim yellow arc shell and a deposit at the upper tip closer to the arc than Pd.

56. Ruthenium gives a bright blue arc core, a yellow arc shell, and a good plating at the upper tip.

57. Platinum gives a bluish arc with a vague green outer edge, and an excessive black deposit on the side of the upper carbon. This is made more marked by addition of rare earths. As with palladium, a lead bead separation can be used.

58. Iridium distills after platinum with a dim bluish carbon arc and deposits at the upper tip closer to the arc than does platinum. The side deposits are less black than those of platinum.

59. Osmium distills after iridium and gives a dim violet carbon arc and sustains the brightest arc crater of any of the platinum metals. The osmium residue (metallic) adheres less to carbon than any other platinum metal. Osmium is the only element in which metal beads can be seen dropping from the upper carbon when viewed in the magnified arc image. The upper carbons receive very slight deposits either on the tip or sides. The best test for osmium in complex mixtures is obtained by using sharply pointed upper carbons which hold the negative craters very steady, in which case the osmium separates as a bead in the center of the crater. Under these conditions the other platinum metals give rings. Osmium boils a little below Ta and W. The platinum metals have been taken out of their distillation order in relation to the following members of this group, in order that they might be considered together.

60. Vanadium distills after chromium but before uranium or titanium carbide. It gives a sharp bright characteristic arc with a reddish-purple core and a thin bright yellow-green arc shell (see Ba) which usually serves to identify vanadium in complex mixtures. Iron can be used to separate V from Ba. The upper carbon with vanadium has a characteristic blue tip and bright yellowish green sides (see Ur). The side color is greatly intensified by boric oxide in the case of complex mixtures containing but little vanadium. The best test for vanadium is the blue ring on the upper tip — obtained by adding 0.2 gr. $BaCO_3$, and 0.01 gr. Al_2O_3 to 0.01 gr. of the vanadium containing material to distinguish it in the presence of Cr, Ti, and Ur. Vanadium in the bead test gives more color with less material than any other element (see Ur).

61. Uranium gives an intense blue arc core with a green inner arc shell and a less bright red outer shell. Even a very little uranium gives scintillating sparks of considerable brightness, which explode with a loud crack. Like vanadium, uranium gives a yellow green deposit on the side of the upper carbon—duller and lower upon the electrode than does vanadium. The best test for uranium in mixtures is made by the addition of rare earth oxides, which causes the usual brown tip deposit on the upper to become almost black (see Pr, Pt). Under the same conditions vanadium gives a blue tip deposit. Vanadium can be separated from uranium by adding both iron and the refractory oxide bead mixture described below. The vanadium dissolves as metal in the iron, and the uranium simultaneously dissolves as oxide in the separate refractory bead.

The refractory bead mix consists of equal parts of barium carbonate, strontium carbonate, calcium oxide, magnesium oxide, silica, alumina, and beryllia. 0.35 g. of this mix is used in the bead tests with from 1 to 50 mg. of uranium material. This mix on heating in a carbon cup gives clear, transparent beads. Addition of a little stannic oxide improves the test for Ur. With from 10 to 50 mg. of iron or chromium there results for a short time a green bead, which becomes colorless on further distillation.

Nickel, manganese, or titanium gives yellow beads behaving in the same manner. Even with minute amount of uranium oxide the green color develops clearly after the iron group metals have been volatilized. The bead is examined after each heating of one minute. Vanadium in fractions of a milligram gives blue beads, but in larger amounts affords black beads. Many other beautiful bead tests can be made with the above mixture.

62. Columbium has a blue arc core with a green arc shell having a red outer portion. The best test for columbium was found in the upper tip deposit which is yellow when hot and white when cold, while that from tantalum is always clear white. This test is duplicated only by Ti or Ce. Columbium distills before tantalum.

63. Molybdenum has a blue arc core with green inner and red outer shell and a green flame tip (see B). Mo gives in the lower cup a characteristic deposit of bluish shiny metallic mirrors, which are easily freed from white oxide. The upper tip is blue-black, often smoking half a minute after stopping the arc—a test peculiar to Mo and sensitive to fractions of a milligram. The sides of the upper carbon are usually white but under some conditions give a red band. With refractory oxides, use 0.2 gr. $BaCO_3$, 0.01 gr. Al_2O_3 and 0.1 gr. of the unknown substance, and observe at the negative tip a bluish dark diffused center spot with sides showing slightly reddish.

64. Tantalum gives a blue arc core with a green arc shell and a red outer portion. Unlike columbium it distills after molybdenum. Unlike columbium the upper electrode tip is very white both hot and cold. In this, it resembles Zr and Th. Tantalum, even in very small amounts has exceptional power of sustaining the brightest and smallest positive craters, with deepest pitting of the carbon. Tantalum has the greatest power of any element of holding back the yellow-green of tungsten.

65. Tungsten gives a dimly colored arc with a bluish arc core and faint green arc shell. With much tungsten, bright craters are secured but smaller amounts of tungsten form as a large, dim circular pool in the positive crater, easily seen in the arc image. It is the only element to give a deposit in the form of a

spot on both the upper and lower tips, which is reddish brown hot and yellow-green cold. By this test, 1/50 milligram of tungsten in half a gram of iron is easily identified at the end of the iron distillation. In a dark room, alkali tungstates in the arc give a garlic odor—with skill, minute amounts of tungsten may be detected. The test must be made in the dark, as light destroys the compound causing the garlic odor. Tungstic oxide is well known to be very sensitive to light. Tungsten is easily identified in any mixture by appearing at the end of the distillation with remarkable delicacy.

VIII. DELICACY OF TESTS.

The delicacy of tests is greatest where ordinary methods, including spectrum analysis, are least effective, especially as regards the very refractory elements. Tests sensitive to 1/50 mg. are given for Ag, Au, and W. Tests sensitive to 1/10 mg. are given for Cd, Fe, Cr, Mo, Ta, most of groups VI and VII, Na, and Li. Tests sensitive to 1 mg. are given for As, groups II, III, IV, and V. Tests sensitive to not less than 10 mg. apply to most of the Class A metals and to K, Rb, and C.

The above refers to the separated elements. In complex mixtures of several materials, the sensitiveness decreases about one fifth. In mixtures, the delicacy increases greatly for the least volatile constituent, as its boiling point is above that of the others. The separation of materials giving very bright arcs is usually promoted by certain addition agents, acting as buffers or prolonging the distillation period. These addition agents should preferably have dim or neutral arcs so as not to interfere with the observation of the materials under test. The same principle applies to the observation of colored upper films. Where materials giving white upper films should be used, tin has the greatest usefulness in this respect. There is a possibility that the bead tests can be refined beyond the milligram stage by optical methods involving multiple reflection.

Any ordinary process of concentration adds, of course, considerably to the delicacy of the arc tests. By using small 6 mm. carbons and currents of 5 amperes instead of 25 amperes the sensitiveness of tests for Class A metals is increased ten times, but the separations are not improved.

Element	No.	Arc Core	Inner Shell	Outer Shell	Chief Peculiarity
Aluminium	36	Violet	Dark space	Green	Popping bead.
Antimony	13	Dim blue	None	None	Orange band, with Cu.
Arsenic	12	Violet	None	None	Garlic odor.
Barium	30	Purple	None	Green	Dim neg. suppressed by Al_2O_3.
Beryllium	37	Violet	Dark space	Green	Last non-cratering oxide.
Bismuth	18	Dim blue	None	None	Green line upper band.
Boron	34	Violet	Dark space	Green	Green flame tip.
Bromine	4	No light			Bromine odor.
Cadmium	14	Dim blue	None	None	Brown oxide with Zn.
Caesium	25	Dim long arcs			Effect on Na_2SO_4 bead.
Calcium	32	Violet	None	Yellow	Red luminescence of oxide.
Carbon		Violet			Subliming black residue.
Cerium	39	Blue	Green	Red	Yellow hot, brown cold tip.
Chlorine	3	No light as element			Band spectra—$BaCl_2$.
Chromium	50	Blue	Green	Red	Brown hot—green cold tip.
Cobalt	47	Blue	Dim yellow		Blue with $Al_2O_3 + Cr_2O_3$.
Columbium	62	Blue	Green	Red	Yellow hot—white cold tip.
Copper	24	Green	None	None	Orange band with Sb.
Erbium	38	Blue green		Green	Green flame tip.
Europium	40	Blue		Orange	Sharp orange arc shell.
Fluorine	2	No light as element			Band spectra—CaF_2.
Germanium	22	Dim bluish		None	Brown tin bead.
Gold	24	Green		None	Purple upper with Sn.
Hydrogen	1	No light			Short initial arc.
Indium		Violet		None	Violet arc—popping bead.
Iodine	5	No light			Violet iodine vapors—odor.
Iridium	58	Bluish		None	Black side after Pt.
Iron	49	Blue		Yellow	Sparks after arc.
Lanthanum	43	Blue	Dark space	Yellow green	Blue inner with Sn.
Lead	17	Dim blue		None	Colors hot and cold upper.
Lithium	29	Blue		Red	Red outside green B.
Magnesium	33	Blue green		Green	Green arc.
Mercury	12	Dim bluish green		None	Uppers with S + CaI_2.

Element	No.	Arc Core	Inner Shell	Outer Shell	Chief Peculiarity
Molybdenum	63	Blue	Green	Red	Smoke upper tip.
Neodymium	41	Blue	Green	Red	With Pr.
Nickel	48	Blue		Dim yellow	White metal beads on tip.
Nitrogen	8	No light as element			Cyanogen spectrum.
Osmium	59	Violet		None	Metal bead sharp tip.
Oxygen	6	No light as element			Many oxide spectra.
Palladium	54	Green		None	Brown side.
Phosphorus	11	No light as element			Odor test—$BaCO_3$.
Platinum	57	Bluish green		Vague green	Black side upper.
Potassium	27	Dim very long arc			Wetting carbon.
Praseodymium	42	Blue	Green	Red	Black tip.
Rhodium	55	Bluish green		Dim yellow	Black upper after Pd.
Rubidium	26	Dim very long arc			Like potassium.
Ruthenium	56	Bright blue		Yellow	Brightest arc of Pt. metals.
Selenium	10	Bluish green		None	Red. ppt. Na_2CO_3 test.
Silicon	35	Violet		Very dim green	Transparent beads.
Silver	20	Green		None	Purple upper with Pb.
Sodium	28	Dim		Yellow	Yellow flame tip.
Strontium	31	Blue		Red	Red arc shell.
Sulphur	7	No light			Odor—Na_2CO_3 test.
Tantalum	64	Blue	Green	Red	Pitting on lowers.
Tellurium	11	Bluish green		None	Dark ppt. Na_2CO_3 test.
Thallium	16	Intense green		None	Intense green arc.
Thorium	45(53)	Blue		Thin red	Last oxide to volatilize.
Tin	21	Dim blue		None	Growth, Sn, Pb + Cu.
Titanium	51	Blue	Green	Red	Yellow hot—white cold tip.
Tungsten	65	Blue	Faint green		Brick color hot, yellow cold tip.
Uranium	61	Intense blue	Green	Red	Black tip with CeO_2.
Vanadium	60	Purple		Yellow green	Blue ring tip.
Yttrium	44	Blue		Intense red	Intense red arc shell.
Zinc	15	Blue		None	Side yellow hot—white cold.
Zirconium	52	Blue	Yellow white	Green	Irregular bright crater.

IX. SEMI-QUANTITATIVE ARC-IMAGE ANALYSIS.

Many of the phenomena are closely related to the amount of material, so that semi-quantitative results can often be arrived at. Colorimetric comparisons of cadmium in zinc are quantitatively successful to within a few percent. The area of green on upper tip in the barium aluminate test for chromium has a definite relation to the amount of chromium. Colorimetric comparisons of beads could probably be applied. The best basis for quantitative results is through the employment of time curves of distillation. This is especially applicable to binary mixtures, as illustrated in curves for iron-alloys in the writer's paper on "Relative Volatilities of Refractory Materials".[5] The curves there given for tungsten can easily be applied to a tungsten ore by using 0.1 g. of ore, 0.1 g. $BaCO_3$, and 0.5 g. of iron. The same principle can be applied in many other cases.

X. CONCLUSIONS.

1. A new method of chemical analysis has been formulated, which consists in bringing the materials to be tested into or under the influence of the carbon arc in a specified manner.

2. The major analytical resources of this method consist in

(a) Characteristic modifications in the appearance and behavior of the arc stream, and of the carbon craters.

(b) The order of distillation of the materials under the influence of the heat of the arc.

(c) The character, color, position, and form of the distillation deposits upon the upper and lower electrodes, and the character of the residues. Also specific modifications of these appearances by addition of suitable reagents.

(d) The application of ordinary analytical reactions to the deposits and residues after decomposition, distillation, or separation by the arc.

3. The method has unique advantages in the analysis of all refractory materials, minerals, and compounds, the decomposition of which is most troublesome and tedious by the usual methods of analysis.

[5] Trans. Am. Electrochem. Soc. (1918), 34, 271.

4. The method has specific analytical advantages in the case of many of the less common elements, and of those offering special difficulties, by present methods. It is of particular value in the case of the following elements, *Fl*, P, *Cd*, Zn, Ag, Au, *Na*, *K*, *Ba*, *Ca*, *Sr*, *Mg*, *B*, *Be*, Al, *Ti*, *Zr*, *V*, *Ur*, *Cb*, *Mo*, *Ta*, *W*, *and the rare earth elements.*

The method is least applicable to the non-metallic elements and is unavailable for acid radicals and organic compounds.

5. The delicacy of test ranges from 1/50 mg. for Ag, Au and W, to 1/10 mg. for S, P, Cd, Pt, Cr, V, Ti, Ur, Yt, Zr, Th, Cb, Mo and Ta. Most of the other elements may be detected in amounts of 1 mg.

The method is least sensitive for the Class A metals, except as mentioned above, and for the following members of Class B, namely, Si, Ni, and the potassium sub-group in the presence of Na.

6. The major constituent of any mineral alloy, refractory, or chemical precipitate, can be easily identified in less than ten minutes.

7. The method of arc analysis automatically registers semi-quantitative results by means of the variations in the duration, intensity, or extent of the identifying arc phenomena.

8. Distinctive tests and a classified and indexed analytical procedure have been outlined for 65 elements.

XI. APPENDIX.

TABLE IV.

Colors of Arc Parts.

Color	Arc Core	Inner Arc Shell	Outer Arc Shell	Flame Tip Above Arc
Red	None	None	Li, Sr, Yt, & all giving inner green shell.*	Li, Cu, Cr
Orange	None	None	Eu	
Yellow	None	None	Na, Fe, CaF_2, TiO_2, SrF_2, Ru, Rh	Na, Ca
Yellow white	None	ZrO_2	ZrO_2, ThO_2,	Mixtures
Yellow green	None	None	Mn, La	Mixtures
Green	Tl, Ag, Cu Au, Pd	Ce, Pr, Nd, V, Cb, Ta, Cr, Mo	Ba, Er, Mg, B, Al Si, Be, Zr, W	B, P, Si, Er, Tl Mo, Cu, Mn
Blue green	Mg, Er, Ni Co, Cr	Cr.	None	
Blue	Most materials	Al, Be, La—with tin	None	Dimly several Class A metals
Reddish purple	Ba, V	None	None	
Violet	C, In, B, Al, Ca, Si, Os, Ir	None	None	
Dark space	(No light non-metals)	B, Al, Be, La	No shell Class A	

* Elements that go through two oxidation steps at very high temperatures often have a green inner arc shell with a red outer edge, and give scintillating sparks.

TABLE V.

Colors of Deposits on Cold Uppers.

Color	Far Up Sides	Colored Band	Negative Tip
Black	C, Pt group, Tl, AgS Hydrocarbons	Co, black glaze B, F, As, and alkalies	Fe, B, Ur, Pr, (Pt with rare earths)
Blue black	Cu with Mn, HgS Pt with ThO_2	Co with Al and Sn	V, Mo
Purple	Pb with *Ag* Sn with *Au*	Co with B_2O_3	Cu tip on standing
Green	Borates of Cr, Cu or Mn, B_2O_3 with Pb and Ag	Pb, Bi, Co with Zn. (Co with Mn with Al and KCl)	Cr Ur with barium aluminate
Greenish yellow	V, Ur	Zn with B_2O_3 Zn with Ni and Co	W
Brown	Cd, Pd, Cu, Au, Ag, with Sb	Cd, Ti Bi at times	Ti, Ge, Zr, Ce, with Ti, Ce with Pr
Yellow to Orange	Fe, Mn, Thallous Iodide, Au, Ag with Bi	Au, Sb with Pb, Sb with Cu, Zn with Ni	Au
Red	P element Se element	Fe, Cd, Cu with B_2O_3 Fe with Cr peculiar red	None
Grey	Hg, Co, complex mixes	Zn with Cu. many complex mixes	Cr with Fe, Ti with Ur
White	Most elements*	SiO_2, P_2O_5, Bi with B_2O_3	La, Yt, Th, Zr Cb, Ta

*** White side deposits are given by As, Zn, Pb, Bi, Sb, Sn, Ni, Cr, Ti, Zr, Th, rare earths, alkalies, alkaline earths, B_2O_3, Cb, Mo, Ta, and W. Metal deposits are given on upper carbons by Hg, Ag, Au, Pt metals and Ni.**

TABLE VI.*

Color When Hot	Color When Cold	Side Bands	Tip of Uppers
Dark brown	Lighter	Fe, Mn, Cd	
Brown	Grey		Cr with Fe
Brown	Green		Cr without iron, Ur with barium aluminate.
Red	Green	Pb, Bi	W (yellow green cold)
Red	Yellow	Zn edge	
Yellow	White	Sb with Bi Al with Sn	Ti, Ce, Cb with white refractory oxides
Yellow	Green	Zn with Co	
Yellow	Brown		CePr, CeTi,
Yellow	Black		CeUr
White	White		Best La, Yt, Th, Zr, Ta

* The above factors enter into the colors of deposit in the lower carbon cup, but so many dark coloring factors are here present that less use can be made of this feature, especially with complex mixtures. The colors hot are best observed about 10 to 15 seconds after breaking the carbon arc. The colors cold appear in one to two minutes in most cases.

The writer takes special pleasure in thanking Mr. H. T. Albers and Mr. J. E. Hrubec for their assistance in carrying out many of the experiments and checking observations. Acknowledgment is no less due Dr. N. K. Chaney and Mr. H. D. Batchelor for helpful comment, and to Dr. Victor Lenher of the University of Wisconsin for several of the rare chemicals used—especially germanium, europium and praseodymium.

DISCUSSION.

W. D. BANCROFT[1]: This is a quite remarkable paper and I hope it will not be too long before the results of it are actually incorporated into analytical data at the universities, because certainly it ought to fit in at a special place.

VICTOR LENHER[2] (*Communicated*): The preceding contribution by Mr. Mott on "Arc Images in Chemical Analysis" is a valuable and interesting contribution. As a scheme of qualitative

[1] Professor of Physical Chemistry, Cornell University.
[2] Professor of Chemistry, University of Wisconsin.

analysis, it shows what can be accomplished by painstaking labor and great patience. It will unquestionably find certain valuable uses. It is indeed astonishing how small quantities of certain of the rarer elements can be detected in a few minutes. Ordinary procedures for a number of these elements require a very long time and the results are commonly uncertain unless the greatest care is taken.

As a study of chemistry at high temperatures, results of the greatest value have been obtained. These results, obtained as they have been with such precision, show the relative volatility of metals and oxides clearly and with such unusual comparisons that will make the results of great value to the worker at high temperatures.

The paper on the whole is a very valuable contribution to the chemistry of high temperatures.

COLIN G. FINK[3]: I should like to ask Mr. Mott whether he has ever carried out any quantitative fractionations of the rare earths? Some rare earths are very difficult to separate chemically, aqueous methods fail, and so do fusion methods; is there any possibility of separating these elements by distillation in the arc?

WM. R. MOTT: I think there is, but I have not tried to follow this up particularly; for instance, take erbium and yttrium—they are rather difficult to separate by the usual means; but with the carbon arc erbium clearly distills first and yttrium last. By adding iron, erbium can still better be separated from yttrium. In complex mixtures of rare earths, thorium oxide always distills last.

There is one other discussion which I happen to have from Dr. Hildebrandt; I will make it very brief. He thinks the arc image method is very complex and suggests that spectrum investigation would be better. I do not need to read it in detail. I will state in answer that we had two experiences in comparing the arc image method with spectrum analysis, in which arc image methods gave better satisfaction. A man, who was supposed to be an expert in spectrum methods, made a photograph for boron in a particular case and did not detect its presence. Later on, I tried

[3] Head of Laboratories, Chile Exploration Co., New York City.

some arc image methods on the same material and instantly detected boron. Then, by taking the spectrum (with the arc) in the ultra violet, the usual beautiful lines for boron were obtained. In another case, a material contained a small percentage of tungsten; by the spectrum method I could not see the tungsten lines, but, on the other hand, I could instantly recognize tungsten by the arc method. It is very simple and satisfactory to recognize tungsten by the carbon tip, which is brick-red when hot and yellow-green when cold.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

PHYSICAL CHARACTERISTICS OF SPECIALIZED REFRACTORIES.[1]

By M. L. Hartmann[2] and O. A. Hougen.[3]

Abstract.

Comparative tests of the resistances of twelve different kinds of refractory bricks to rapid cooling by an air blast after heating to 1350° C. This was repeated up to ten treatments with nine bricks, while three were completely disintegrated at the seventh, fourth and third treatment. The percentage loss of weight is stated, which varied from 0.3 percent with bonded carborundum (carbofrax C) to 100 percent with the last three samples.

[J. W. R.]

Part I.—Spalling Losses.

Most refractory bricks when subjected to sudden changes of temperature or to excessive strain at high temperatures break and shell off in various ways and in different amounts. This effect is noted particularly when only one face of a brick is heated. In the arches of furnaces, a pinching effect often takes place due to sudden changes in temperature which results in disrupting the brick. Such action may cause complete destruction of a furnace. This disrupting action is commonly known as spalling. Almost all refractories exhibit spalling, the different materials showing wide variation in the magnitude of this effect.

Spalling is due chiefly to three causes:

(a) Expansion or contraction of individual grains due to temperature changes.

(b) Change of crystalline structure.

(c) Chemical reactions within the structure.

[1] Manuscript received March 3, 1920. This and the following paper record the results of portions of a general investigation aiming to contribute some definite and accurate information concerning the physical properties of special refractory bricks as compared with the more common fireclay refractories.

[2] and [3] Research Laboratory, Carborundum Co., Niagara Falls.

Magnesia and silica refractories show excessive spalling losses in practice. Spalling of magnesia brick is due chiefly to the conversion of "A" Magnesia to the "B" form,[4]. In silica brick, spalling is due chiefly to the conversion of quartz to tridymite and cristobalite.[5] Fire bricks usually contract upon heating, due mainly to the closing of pores by the fusion or sintering of portions of the bond rather than to any crystallographic conversion.

Spalling has usually been reported in general terms as the result of actual furnace operation. No figures showing actual comparison of the spalling of different bricks under the same conditions are available in the literature. To obtain comparable results in commercial installations would be exceedingly expensive and time consuming, and hence a more rapid test is needed for procuring comparable data.

Some previous work has been done on this by Nesbitt and Bell.[6] The bricks to be tested were heated at 1350° C. for one hour in the doorway of a furnace, with one end flush with the interior wall. They were then removed and cooled rapidly by immersion of the heated end to a depth of 4 inches in a fixed amount of water for three minutes. This operation was repeated ten times for each brick, and the final results reported in percentage loss (by weight) of material which had broken off.

Nesbitt and Bell also tried the method of rapidly cooling in a blast of air, but adopted the water quenching method because it seemed to give more rapid cooling and consequently the spalling effect was augmented.

However, there are many objections to the quenching method as a general method: (1) It is applicable only to fireclay bricks. (2) In practice, bricks are never subjected to similar treatment. (3) The water has a disruptive action on porous bricks by seeping into the pores and forming steam. (4) Water at 1300° C. reacts chemically with some materials; this is especially noticeable with magnesia and carborundum bricks.

[4] J. W. Mellor, Trans. Eng. Ceramic Soc. (1917), 16, 85-100.
[5] D. W. Ross, "Silica Refractories," U. S. Bureau of Standards, Technologic Paper (1919).
[6] Chem. & Met. Eng. (1916), 15, 210; Proc. Am. Soc. Test. Mat. (1916), 16, 350.

FIG. 1. Furnace Front used in Spalling Tests.

FIG. 2. Carbofrax "C" Bricks After Test.

FIG. 3. Carbofrax "A" Bricks After Test.

FIG. 4. Carbofrax "B" Bricks After Test.

FIG. 5. Grade "A" Fireclay Bricks After Test.

FIG. 6. Recrystallized Carborundum Bricks After Test.

FIG. 7. Natural Zirconia Bricks After Test.

FIG. 8. Grade "B" Fireclay Bricks After Test.

FIG. 9. Comparative Average Spalling Loss of Refractory Bricks.

1. Carbofrax "C." 2. Carbofrax "A." 3. Carbofrax "B." 4. Grade "A" Fireclay. 5. Recrystallized Carborundum. 6. Bauxite. 7. Zirconia (natural). 8. Grade "B" Fireclay. 9. Grade "C" Fireclay. 10. Chrome. 11. Silica. 12. Magnesia.

Revised Air-Blast Method.

Preliminary tests showed that almost as severe results were obtained by the air-blast as by the quenching method. For example, the average spalling loss on Grade B fireclay by water quenching was 79 percent and by the air-blast method it was 65 percent. The quenching method used was identical with that of Nesbitt and Bell.

The air-blast method finally adopted for our work was as follows: The bricks to be tested were thoroughly dried at 110° C., weighed and heated in the openings of the front wall of a specially designed oil-fired furnace, with ends flush with the inside walls.

The furnace construction is shown in Fig. 1. The front wall was constructed of recrystallized carborundum bricks, with twelve openings 2¾ in. x 4¾ in. (7 cm. x 12 cm.) in which the bricks under test were inserted with the end flush with inner wall of the furnace. This allowed only one end of the brick to be heated. The use of a neutral highly refractory brick as a support prevents sticking of the brick under test. Freedom from sticking is very important, because when the bricks under test adhere to the furnace bricks large pieces of the somewhat weakened test brick may be broken loose by the force required to pull the brick from the furnace. The front wall was insulated with firebrick to prevent excessive heat losses. When the temperature of the furnace reached 1350° C. the bricks were inserted in the openings of the wall, and each brick left in the furnace for one hour. Each brick was then taken out and set on the cold end with the hot end exposed to an air blast for 15 minutes. This operation was repeated ten times for each brick. The blast was supplied by a ¾-in. (2 cm.) hose delivering air at the rate of about 27 cubic feet (0.76 cu. m.) per minute. This amount of air apparently produced nearly as rapid cooling as quenching in water. Examinations of the bricks were made at the end of each cooling, to detect the developments of checks, cracks or spalling. At the end of the final cooling all particles which could be easily broken off by the fingers were removed. The bricks were weighed and the percentage loss calculated from the original weight.

The behavior of the various bricks during test considered in order of their resistance to spalling are given below. In making

comparisons it must be borne in mind that while the percentage weight of material broken off by spalling is important, the manner of spalling and the final condition of the brick after the test must be considered.

(1) Bonded carborundum brick (Carbofrax C). The spalling was negligible, the slight loss of 0.3 percent being due to abrasion in handling. These bricks contain about 95 percent carborundum. Very faint check lines were visible while the bricks were hot, but there were no visible cracks after the final cooling. (See Fig. 2.)

(2) Bonded carborundum brick (Carbofrax A). The losses by spalling usually occur by the breaking off of large pieces. This was more or less irregular, a few bricks showing high spalling and others showing practically no spalling. Small check lines were visible on the bricks after the test. The average percentage spalling of nine bricks was six percent. (Fig. 3.)

(3) Bonded carborundum bricks (Carbofrax B), containing about 90 percent silicon carbide gave an average spalling loss of 8 percent. The losses occurred usually in large pieces, although there was also some spalling in small fragments. The bricks were badly checked after the test. (Fig. 4.)

(4) Grade A fireclay bricks (apparent density 1.78) very coarse in texture, gave a spalling loss of 9 percent. Spalling was uniform. It did not occur by large pieces shelling off but rather in the separate crumbling off of the coarse grains. Some fine check lines were visible in the bricks after testing. (Fig. 5.)

(5) Recrystallized carborundum bricks (Refrax). These bricks are composed entirely of carborundum, held together by the intergrowth of crystals. No bonding material is used. The average spalling loss amounted to 12 percent. The spalling occurred in the form of medium-sized pieces. Most of the spalling occurred during the first few coolings. Only a few short cracks were visible after the test. (Fig. 6.)

(6) Bauxite bricks, of a well-known make, coarse in texture (apparent density 1.91) gave an average of 43 percent spalling loss. These bricks showed a very peculiar and unaccountable behavior, practically the whole loss occurring at the fifth heating, little spalling occurring either before or after. Fine check lines were visible after the test.

(7) Zirconia bricks, made of commercial natural zirconia, and containing approximately 80 percent zirconium oxide. Average spalling loss amounted to 53 percent. Many large cracks developed and large pieces broke off during the test. The spalling and cracking was about equal in all of the bricks tested. (Fig. 7.)

(8) Grade "B" fireclay bricks (apparent density 2.04). This variety has a close-grained texture. The bricks had an average spalling loss of 65 percent. There were large variations in the results, as shown by Fig. 8.

(9) Grade "C" fireclay bricks (apparent density 2.09), of very dense, close-grained texture, showed a spalling loss of 90 percent.

(10) Chrome bricks (apparent density 2.83), of standard make, coarse grained, were completely shattered at the end of the 7th cooling. Compared with other kinds of bricks which stood up through the ten heats, this is equivalent to a spalling of 155 percent. The pieces of bricks became very soft, and could be easily broken.

(11) Silica bricks (apparent density 1.66) of lime-bonded standard make, gave very excessive spalling, being complete at the end of the 3d and 4th cooling, equivalent to 225 percent on the basis of ten coolings.

(12) Magnesia bricks (apparent density 2.27), a dense fine-grained brick of standard make. These bricks exhibited complete spalling at the end of the 3d cooling, equivalent to 375 percent on the basis of ten coolings. They became very soft and fragile at 1350° C., making them very difficult to handle without breaking.

CONCLUSIONS.

The results of all tests are summarized in the following table and comparative results shown graphically in Fig. 9.

	Percent	
1. Bonded Carborundum (Carbofrax C)	0.3	at end of 10th cooling
2. Bonded Carborundum (Carbofrax A)	6	at end of 10th cooling
3. Bonded Carborundum (Carbofrax B)	8	at end of 10th cooling
4. Grade A Fireclay	9	at end of 10th cooling
5. Recrystallized Carborundum (Refrax)	12	at end of 10th cooling
6. Bauxite	43	at end of 10th cooling
7. Zirconia (natural)	53	at end of 10th cooling
8. Grade B Fireclay	65	at end of 10th cooling
9. Grade C Fireclay	90	at end of 10th cooling
10. Chrome	100	at end of 7th cooling
11. Silica	100	at end of 4th cooling
12. Magnesia	100	at end of 3rd cooling

In general, coarse-grained bricks and bricks of high porosity show least spalling losses.

Without exception, all bricks show some checking when subjected to sudden cooling. These check lines are always visible during the first cooling, subsequent coolings render these checkings more visible and usually they develop into cracks and spallings. In the case of carborundum bricks checking is usually visible only when hot.

All bricks lose their sound, metallic ring after quenching or air-cooling.

From five to ten bricks were used in each test. These were purchased in the open market and undoubtedly do not give absolute results for the various types of refractories. The general order of magnitude of spalling is probably correct, however, and inasmuch as no results of similar tests have been previously published, these preliminary results may be of value.

Research Laboratory, The Carborundum Company,
Niagara Falls, N. Y., February 15, 1920.

DISCUSSION.

F. A. J. FITZGERALD[1]: The spalling which was found in the case of the magnesia bricks was undoubtedly due to change of crystalline structure. If the magnesia bricks had been made of electrically sintered magnesite the spalling would have been far less, for the increase in absolute density of amorphous magnesia when calcined is progressive till the melting point is reached.

By "chemical reactions within the structure" do the authors mean chemical reactions which occur in the brick itself?

The test in which the brick is first heated and then chilled by turning on an air blast is hardly sufficient in the case of refrax bricks subject to high temperature in a strongly oxidizing atmosphere, for under such circumstances there is apt to be progressive oxidation of the silicon carbide to silica and subsequent spalling.

R. M. HOWE[2] (*Communicated*): The writer is of the opinion that the objections given on page 708 with respect to the quenching

[1] FitzGerald Laboratories, Inc., Niagara Falls, N. Y.
[2] Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

test might be modified, although there is no doubt but that the quenching test is most applicable to fireclay and other bricks that are capable of withstanding a great number of rapid temperature changes. Nesbitt and Bell have already indicated that the more rapid quenching test gives results which are roughly proportional to those obtained by cooling in air, and this statement has been verified in this laboratory. Consequently, the use of water as a cooling medium is a decided advantage when materials such as 1, 2, 3, 4 and 5 are being studied, for when they are cooled in air the task is almost endless.

However, when bricks, such as 6, 7, 8, 9, 10, 11 and 12 are being studied a less severe test is necessary because with its adoption a finer distinction may be obtained between materials which spall readily. Even repeated heating and cooling, without the use of an air blast, is sufficient to cause those materials to spall. Because of these facts the writer believes that both the quenching and air blast methods of cooling have their applications.

In practice bricks are sometimes, but not usually, subjected to the influence of cold water, although the furnace gases invariably contain an appreciable amount of steam. Consequently, any chemical, disruptive, or similar action which might result from cooling in water will probably take place when the water vapor of the furnace gases comes in contact with the heated brick.

The statement regarding the chemical action between water and either magnesia or carborundum bricks at 1,300° C. is interesting, and the writer would like to ask what this action is, whether it is noted when the water vapor in the combustion gases at 1,300° C. is in contact with the brick, and if not, why?

R. D. PIKE[1] (*Communicated*): Under conclusion No. 12, the authors state that a dense, fine grain magnesite brick of standard make became very soft and fragile at 1,350° C., making it very difficult to handle without breaking.

The work of McDowell & Howe ("Basic Refractories for the Open Hearth," Bulletin 146, American Institute of Mining Engineers, February, 1919, page 306), shows that standard makes of magnesite brick failed abruptly by shearing when loaded to the extent of 25 lb. per sq. in. (1.75 kg. per sq. cm.) on end, at a temperature of 1,555° C. It is quite apparent from a reproduc-

[1] Consulting Chemical Engineer, San Francisco, Calif.

tion of the photograph of the brick tested, that in this particular case the brick had not become softened up to the temperature of 1,555° C.

H. G. Schurecht, in an article entitled "A Machine for Testing the Crushing Strength of Firebricks," Journal of American Ceramic Society, Vol. 2, No. 8, page 606, gives a curve showing that a magnesite brick when heated to about 1,355° C. failed by compression on end at 415 lb. per sq. in. (30 kg. per sq. cm.), which of course would indicate that the brick was anything but soft at this temperature.

I would be glad to have this apparent discrepancy cleared up.

M. L. HARTMANN (*Communicated*): In reply to Mr. FitzGerald's question, the expression "by chemical reactions within the structure" should read "within the brick."

Referring to Mr. FitzGerald's comments concerning the spalling of recrystallized carborundum brick, the tests described in the paper are intended to give the relative spalling tendencies in the specimens tested. If information is desired about the spalling of a recrystallized carborundum brick after it has been oxidized by very long exposure to high temperature in an oxidizing atmosphere, this could be obtained by the use of the described method upon a brick after it had been oxidized.

The objections given on page 708 to quenching apply, of course, only to its use as a general method. The whole object of our paper was to show the relative tendencies to spall of the different classes of refractory bricks which are in common use. For this purpose it was necessary to select that method of cooling which would not be too disruptive for the high spalling bricks such as silica and magnesia, and yet one which would show differences between classes of refractories with very small tendency to spall. A further consideration was the violent disruptive effect of immersing hot magnesia and carborundum bricks into cold water. This effect is probably due either to the chemical action between the water and magnesium oxide or the silicon carbide at the high temperature, or to the extremely rapid generation of steam within the pores of the brick, causing very rapid expansion of the gases. We do not know of any cases in which this effect has been observed from the water vapor in the combustion gases in contact with linings of these materials. Under such conditions, a much

smaller effect would be expected in any case, because of the smaller surface exposed, and the fact that surface glazing prevents penetration of gases and vapors.

The discrepancy pointed out by Mr. Pike is probably due to the fact that magnesia bricks of different manufacturers vary greatly in properties. The statement made on page 711 that "they became very soft and fragile at 1,330° C., making them very difficult to handle without breaking" means that the particles were apparently loosely bound together at this temperature, and not that the brick was melting. It may be of interest to add that a magnesia brick of the same make as used in this test has since been tested in this laboratory, and shears abruptly at 1,500° C. under a load of 25 pounds per square inch.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

PHYSICAL CHARACTERISTICS OF SPECIALIZED REFRACTORIES.[1]

By M. L. Hartmann[2] and J. F. Kobler.[3]

Abstract.

Tests on different kinds of refractory materials, at ordinary temperatures and at 1350° C., made by a carborundum cutting wheel under a constant pressure, and measuring the depth abraded in a given time. The results are accurate relatively and qualitatively, but only roughly so quantitatively. They are sufficiently reliable to indicate the general relative resistances of these materials to abrasion in practical use. [J. W. R.]

Part II.—Comparative Cold and Hot Abrasion Tests.

In certain furnace operations, the resistance of the furnace materials to abrasion is very important. In blast furnaces, retorts, roasting furnaces, coke ovens, and crucibles the charging, discharging, and movement of the load tend to wear away the refractory. In blast furnaces the downcoming charge tears away as much as ten inches of firebrick construction in one year. In coke ovens, regenerators, hot stoves, and flues, abrasion is caused by flue dust.

High resistance to abrasion is secured by means of a close, hard and well-burned surface. In firebrick the greatest resistance to abrasion is secured by using a bond which vitrifies readily. Hard-burned bricks are most suitable for resisting abrasion. The surfaces of retorts are often glazed in order to decrease abrasion. Crucibles with a coarse surface wear away more rapidly than when the surface is dense and fine grained. On the other hand, with increased density and fineness of texture the tendency to crack and spall is increased.

[1] Manuscript received March 3, 1920.

[2] and [3] Research Laboratory, Carborundum Co., Niagara Falls.

Bauxite, when burned at high temperatures, has proved in actual practice to resist abrasion better than other common refractories. Magnesia and chrome bricks become soft and friable at high temperatures and are abraded rapidly.

Methods of Testing Abrasion.

Various schemes have been proposed for testing abrasion. In one method, a Bauschinger grinding machine is used,[4] the bricks are held on a revolving plate under a constant pressure for a given period. This method is not applicable for testing hot bricks.

The standard rattler test for wearing, and the sand blast methods, are adapted especially for paving bricks.

The method used in the present tests is that proposed by Nesbitt and Bell[5] with slight modifications. In this method the bricks were abraded by a carborundum grinding wheel running at a constant speed with the bricks maintained at a constant pressure. The bricks were tested both hot and cold.

The samples were prepared for the test by cutting a groove on each end to fit the testing wheel. The groove was cut so deep that the maximum area was exposed to the cutting action of the wheel. The depths of the cuts were then measured by a depth micrometer. The bricks were abraded cold for five minutes on each end and re-measured with a depth micrometer. The difference in depth represents the abrasion in linear inches for a five-minutes period.

For testing hot, the bricks were placed in a furnace for two hours at a temperature of 1350° C. The furnace used for heating was the same as used for spalling tests. (See previous article). Holes were provided for inserting the bricks so that only one end was heated at a time. Before inserting the bricks the furnace was heated to 1350° C. After heating, the bricks were removed quickly and while still hot were held against the wheel for three to five minutes, the actual time being determined by a stop watch. When cold the cuts were re-measured. The differences in measurements referred to a five-minute period represented the abrasion. The test was repeated on the opposite end.

[4] Havard, Refractories and Furnaces, p. 260.

[5] Chem. & Met. Eng. (1916), 15, 210; Proc. Am. Soc. Test. Mat. (1916), 16, 368.

FIG. 1. Abrasion Testing Machine.

The wheel used in testing was a 12-in. (30 cm.) carborundum wheel, Grit 16, Bond G-5; Grade I; 1 in. (2.5 cm.) arbor; 2 in. (5 cm.) face; speed of revolution 512 r. p. m.—average peripheral velocity 1560 feet (468 m.) per minute. The brick was held against the wheel by a swinging table adjusted so as to maintain a pressure of 25 pounds (11.4 kg.) against the wheel (Fig. 1). It was necessary to re-dress the wheel very frequently.

According to the tests made, the relative order of the bricks in resisting abrasion is as follows:

Tested as received, cold (5-minute period)

	Inches	Mm.
1. Bonded carborundum (Carbofrax C)	0.01	0.25
2. Recrystallized carborundum (Refrax)	0.01	0.25
3. Bonded carborundum (Carbofrax B)	0.02	0.50
4. Bonded carborundum (Carbofrax A)	0.02	0.50
5. Zirconia (natural)	0.02	0.50
6. Bauxite	0.02	0.50
7. Grade C Fireclay	0.05	1.25
8. Magnesia	0.05	1.25
9. Chrome	0.07	1.75
10. Silica (lime bonded)	0.17	4.25
11. Grade B Fireclay	0.25	6.25
12. Grade A Fireclay	0.26	6.50

Tested Hot (1350° C. at start) (5-minute period)

	Inches	Mm.
1. Bonded carborundum (Carbofrax C)	0.01	0.25
2. Bonded carborundum (Carbofrax A)	0.01	0.25
3. Bonded carborundum (Carbofrax B)	0.03	0.75
4. Bauxite	0.04	1.00
5. Zirconia (natural)	0.06	1.50
6. Recrystallized carborundum (Refrax)	0.07	1.75
7. Grade C Fireclay	0.07	1.75
8. Grade B Fireclay	0.09	2.25
9. Grade A Fireclay	0.11	2.75
10. Chrome	0.27	6.75
11. Magnesia	12.5	313.
12. Silica (lime bonded) spalled too badly for measurement.		

Fireclay bricks apparently increase in toughness or resistance to abrasion when heated. This is probably due to the fact that at 1350° C. the fireclay starts to fuse and becomes sticky and fills up the open spaces in the grinding wheel.

Special tests were made of the effect of hard burning of bricks on the abrasion at ordinary temperatures. This was found to greatly increase the toughness in all types of clay-bonded bricks,

increasing that of fireclay bricks as much as twenty times. On the clay-bonded carborundum bricks this increase of toughness was slight, probably because in the manufacture of these bricks they are heated to an equally high temperature.

It should be pointed out that final conclusions should not be drawn from the above results, although the relative values are probably not displaced. The variation in the different tests on the same type brick was in many cases quite large, which would necessitate a large number of determinations of abrasion to get a true average value for a given brand. In addition to this, there is the variation in the product from one manufacturer from time to time and from different manufacturers. For this reason we have not undertaken to determine the true average abrasion of bricks of a given material by testing large numbers of samples, but have intended in the results to show merely the general character of the resistance to abrasion at ordinary temperatures and at 1350° C., of the common types of refractories.

Research Laboratory, The Carborundum Company,
Niagara Falls, N. Y., February 11, 1920.

DISCUSSION.

F. A. J. FITZGERALD[1]: The abrasive tests are interesting; but would it not give a better test if, while the bricks were heated, a sand blast were turned on them? I remember a long time ago when working for Dr. Acheson, when he was experimenting with his siloxicon refractories, one of the most difficult refractory problems was that found in the use of pulverized coal as a fuel, the abrasion from the ash being very severe. The sand blast would imitate closely an abrasive action of this kind.

S. A. TUCKER[2]: Could not that test be carried out by heating the brick electrically, since it should be a conductor at high temperatures?

[1] FitzGerald Laboratories, Inc., Niagara Falls, N. Y.
[2] Columbia University, New York City.

F. A. J. FITZGERALD: The bricks could have a hole drilled in them and through this could be passed a carbon resistor which would heat the bricks while the sand blast was turned on them.

M. L. HARTMANN (*Communicated*): We do not believe that the method of sand blasting the bricks at 1,350° C. would be as satisfactory as the method of grinding on an abrasive wheel, because (1) the action of the sand blast would be very much slower, and the test would have to be continued for a long time, and (2) the fine dust particles of sand or brick would stick to the brick surface at this temperature, probably developing a glaze which would be of different resistance to abrasion than the brick itself.

A paper presented at the Thirty-seventh General Meeting of the American Electrochemical Society, in Boston, April 8, 1920, President Bancroft in the Chair.

THE ADSORPTION OF ARSENIOUS OXIDE BY METASTANNIC ACID.[1]

By T. R. Briggs[2] and W. J. Bartlett.[3]

Abstract.

Tests were made to determine the influence of temperature on the adsorption of arsenious oxide from solution by metastannic acid. The adsorption equilibrium is found to be reached rapidly, even at ordinary temperatures, and is reversible. The adsorbed oxide has a "peptizing" effect on the acid. The adsorption takes place in presence of sulphuric acid and copper sulphate, thus explaining Gruessner and Badt's method of removing arsenic from spent copper refinery electrolyte. At higher temperatures adsorption decreases. No evidence has yet been found for the formation of definite arsenites. [J. W. R.]

In a paper on the electrolytic refining of copper, Addicks[4] has referred to the use of metastannic acid in removing arsenious oxide from impure or spent electrolyte. On treating arsenical copper sulphate solutions with metastannic acid, especially on boiling, the arsenic is more or less removed and forms, apparently, an insoluble compound with the stannic oxide, from which the latter may be regenerated for further use. The process forms the subject of two patents[5] by Gruessner and Badt, in whose specifications mention is made of a compound between the arsenic and the metastannic acid, though no attempt is made to assign to this compound any definite composition.

[1] Manuscript received March 3, 1920.
[2] Department of Chemistry, Cornell University.
[3] Cornell University.
[4] Jour. Franklin Inst. (1905), 160, 423.
[5] U. S. Pat. (1893), 489632 and 489633.

In view of the fact that Biltz[6] proved definitely that the removal of arsenic from solution by hydrous ferric oxide is a case of adsorption and that no definite arsenites are formed, at least not under the conditions that Biltz was working with, the present authors were led to suspect that the metastannic acid-arsenious oxide reaction was also one of adsorption. In this paper are presented results which confirm this conjecture and which throw light upon the question of the arsenites of tin. Further experiments are in progress.

Reichard[7] has prepared and described several so-called arsenites of tin. When potassium acid arsenite is added to a dilute solution of stannic chloride a compound $2As_2O_3.5SnO_2$ is apparently precipitated, though no proof is offered that this compound is a real one. When hydrous stannic oxide is boiled with a solution of arsenious oxide plus sodium hydroxide "the stannic acid remains unchanged." When neutral sodium arsenite ($Na_2AS_2O_4$) is added to stannic chloride, a voluminous white precipitate of the composition $Sn_7As_2O_{17}$ ($As_2O_3.7SnO_2$) results. Reichard left the problem in an obviously unsatisfactory condition.

EXPERIMENTAL.

The hydrous stannic oxide (metastannic acid) used in this work was prepared[8] by treating block tin with hot aqueous nitric acid (sp. gr. 1.4). The material was washed many times by decantation, and when litmus showed it to be entirely free from acid, it was added to water in a bottle and used throughout in the form of a milky suspension. The different solutions of arsenious oxide were made by diluting a concentrated solution as desired and each was analyzed in duplicate.

Arsenic was determined volumetrically with standard iodine after neutralizing and adding sodium bicarbonate in excess. When copper sulphate was present together with free sulphuric acid, the latter was neutralized with bicarbonate and copper was precipitated as the oxalate in acetic acid solution. Arsenic was

[6] Berichte (1904), 37, 3138; *Cf.* also Reychler: Jour. Chim. phys. (1909), 7, 362; Blitz: *Ibid.* (1909), 7, 570; Lockemann and Paucke: Zeit. Kolloidchemie (1911), 8, 273; Lockemann and Lucius: Zeit. phys. Chem. (1913), 83, 735.

[7] Ber. deutsch. chem. Ges. (1894), 27, 1019; (1897), 30, 1915; (1898), 31, 2168.

[8] By Mr. W. A. Papke, in this laboratory.

then determined as usual. Special experiments showed that copper oxalate carries down little or no arsenic.

The experiments were carried out as follows: 25 cc. of arsenious oxide solution and 5 cc. of stannic oxide suspension were mixed in small glass stoppered bottles. The suspension was pipetted out of the stock bottle, care being taken to shake thoroughly just prior to removing the sample. The stannic oxide content of the latter was determined by direct gravimetric analysis. The actual volume of the stannic oxide never exceeding 0.2 cc., it was neglected and the volume of the solution in each bottle was taken to be 30 cc.

The bottles were set aside at room temperature—approximately 21° C.—or at higher temperatures in a water thermostat.

The time necessary for the system to reach a stationary state was determined as follows: Into a large glass-stopped bottle were placed 300 cc. of a solution of arsenious oxide (8.84 mg. per cc.) and 60 cc. of stannic oxide suspension. The bottle with its contents was shaken from time to time and at definite intervals samples of the solution phase were removed for analysis. The following data were obtained:

Temperature 21°C (approximately)

Time Hours		As_2O_3 in Solution Milligrams per cc.
after	1	5.38
	2	4.81
	3	4.74
	4	4.74
	5	4.71
	6	4.73
	9	4.69
	10	4.70

In the experiments which follow, each set of bottles was allowed to stand at least 24 hours with oft-repeated and thorough shaking. As equilibrium is reached in less than 5 hours even at 21° C., this interval of time (24 hours) was considered to be ample. At the end of this interval, the stannic oxide was allowed to settle without change of temperature and the arsenic was determined in the clear solution. Arsenious oxide removed from solution was determined by difference and was assumed to be arsenious oxide in the solid phase.

TABLE I.

Metastannic Acid, Arsenious Oxide and Water.

Temperature 21°C (approximately)

$$\left(\frac{x}{m}\right)^{5.33} = 0.00224\ c.$$

Milligrams As_2O_3			Liquid Phase	Solid Phase	x/m calculated
In Original Solution 30 cc.	In Solution After Adsorption	Adsorbed by SnO_2 (395 mg.)	Millimols. As_2O_3 per liter = c × 10^3	Mols. As_2O_3 per mol. SnO_2 = x/m	
20.0	1.0	19.0	0.17	0.037	0.064
32.5	2.0	30.5	0.34	0.059	0.071
52.7	6.5	46.2	1.09	0.089	0.088
82.2	25.0	57.2	4.21	0.110	0.113
105.4	41.8	63.6	7.05	0.123	0.125
131.8	61.1	70.7	10.3	0.136	0.134
170.6	95.0	75.6	16.0	0.146	0.149
200.7	117.7	83.0	19.8	0.160	0.152
262.4	176.8	85.6	29.8	0.165	0.164
335.7	248.7	87.0	41.9	0.168	0.174
407.6	318.6	89.0	53.7	0.172	0.183
464.0	373.5	90.5	62.9	0.174	0.188

TABLE II.

Metastannic Acid, As_2O_3 and Water. Mechanical Shaker.

Temperature 21°C (approximately)

$$\left(\frac{x}{m}\right)^{5.6} = 0.00123\ c.$$

Milligrams As_2O_3			Liquid Phase	Solid Phase	x/m calculated
In Original Solution 30 cc.	In Solution After Adsorption	Adsorbed by SnO_2 (395 mg.)	Millimols. As_2O_3 per liter = c × 10^3	Mols. As_2O_3 per mol. SnO_2 = x/m	
20.0	1.0	19.0	0.17	0.037	0.064
32.5	2.2	30.3	0.34	0.058	0.072
52.7	6.3	46.4	1.06	0.089	0.089
82.2	24.4	57.7	4.11	0.111	0.113
105.4	38.8	66.6	6.53	0.127	0.123
131.8	59.7	72.1	10.1	0.139	0.133
170.6	94.9	75.7	16.0	0.146	0.145
200.7	123.1	77.6	20.7	0.150	0.151
262.4	178.4	84.0	30.0	0.162	0.162
335.7	247.1	88.6	41.6	0.171	0.171
407.6	318.0	89.6	53.6	0.173	0.179
464.0	368.5	95.5	62.1	0.184	0.184

The first series of measurements was made at room temperature with solutions containing only arsenious oxide. The bottles were shaken at intervals by hand. 395 milligrams of SnO_2 were present in each bottle. The data form Table I.

The second series was a repetition of the first, except that the bottles were shaken in a machine for many hours. The numbers form Table II. It is apparent that no especial difference in results followed the use of the mechanical shaker.

The third series was carried out at 45° C. in a thermostat with shaking by hand. The results appear in Table III.

TABLE III.

Metastannic Acid, As_2O_3 and Water.

Temperature 45°C.

Milligrams As_2O_3			Liquid Phase	Solid Phase
In Original Solution 30 cc.	In Solution After Adsorption	Adsorbed by SnO_2 (395 mg.)	Millimols. As_2O_3 per liter = c × 10^3	Mols. As_2O_3 per mol. SnO_2 = x/m
20.0	1.7	18.3	0.29	0.035
32.5	3.0	29.5	0.51	0.058
52.7	8.5	44.2	1.43	0.085
82.2	26.6	55.6	4.48	0.107
105.4	44.1	61.3	7.43	0.118
131.8	70.3	61.5	11.80	0.119
170.6	97.0	72.6	16. 3	0.139
200.7	127.5	73.2	21.5	0.141
262.4	187.2	75.2	31.5	0.145
335.7	255.9	79.8	43.1	0.154
407.6	332.5	75.1	56.0	0.145
464.0	388.3	75.7	65.4	0.146

In the fourth series the solutions of arsenious oxide were acidified with sulphuric acid (100 g. per liter). The data form Table IV.

The fifth series was performed with a somewhat different stock suspension of stannic oxide and is perhaps not quite comparable with the four series preceding. The solutions of arsenious oxide contained both sulphuric acid (100 g. per liter) and copper sulphate (100 g. per liter) and therefore might be considered to represent an impure electrolyte of the copper refinery. 620

milligrams of stannic oxide were present in each bottle. The data appear in Table V.

TABLE IV.

Metastannic Acid, As_2O_3, H_2SO_4 and Water.

Temperature 21°C (approximately)

$$\left(\frac{x}{m}\right)^3 = 0.0257\ c.$$

Milligrams As_2O_3			Liquid Phase	Solid Phase	x/m calculated
In Original Solution 30 cc.	In Solution After Adsorption	Adsorbed by SnO_2 (395 mg.)	Millimols. As_2O_3 per liter = c × 10^3	Mols. As_2O_3 per mol. SnO_2 = x/m	
20.0	6.4	13.6	1.01	0.026	0.030
32.5	14.3	18.2	2.20	0.035	0.039
52.7	27.9	24.8	4.41	0.048	0.048
82.2	51.8	30.4	8.18	0.059	0.059
105.4	73.8	31.6	11.8	0.061	0.067
131.8	92.6	39.2	14.6	0.076	0.072
170.6	128.7	41.9	20.3	0.081	0.081
200.7	155.8	44.9	24.6	0.087	0.086
262.4	213.5	48.9	33.7	0.094	0.095
335.7	281.9	53.8	44.5	0.104	0.105
407.6	353.3	54.3	55.8	0.105	0.113
464.0	408.0	56.0	62.4	0.108	0.117

TABLE V.

Metastannic Acid, As_2O_3, H_2SO_4, $CuSO_4$ and Water. 100 g H_2SO_4 Per Liter; 100 g $CuSO_4$ Per Liter.

Temperature 30° C.

Milligrams As_2O_3			Liquid Phase	Solid Phase
In Original Solution 30 cc.	In Solution After Adsorption	Adsorbed by SnO_2 (620 mg.)	Millimols. As_2O_3 per liter = c × 10^3	Mols. As_2O_3 per mol. SnO_2 = x/m
15.4	5.0	10.4	0.84	0.013
40.4	12.5	27.9	2.1	0.034
82.9	39.1	43.8	6.6	0.054
115.5	60.5	55.0	10.2	0.068
172.5	101.2	71.3	17.0	0.088
207.2	120.9	86.3	20.5	0.106
334.7	242.2	92.5	40.8	0.114
407.7	303.1	104.7	49.9	0.129
485.7	372.8	112.9	62.7	0.139

A sixth series was carried out at 99° C. by placing the arsenious oxide-stannic oxide-water mixtures in sealed tubes and heating one week in a bath of boiling water. The results form Table VI.

TABLE VI.

Metastannic Acid, As_2O_3 and Water.

Temperature 99° C.

Milligrams As_2O_3			Liquid Phase	Solid Phase
In Original Solution 30 cc.	In Solution After Adsorption	Adsorbed by SnO_2 (410 mg.)	Millimols. As_2O_3 per liter = c × 10^3	Mols. As_2O_3 per mol. SnO_2 = x/m
20.0	4.3	15.7	0.72	0.034
32.5	6.9	25.6	1.2	0.048
47.6	10.1	37.5	1.7	0.069
52.7	13.8	38.9	2.3	0.072
66.0	23.8	42.2	4.0	0.078
82.2	31.5	50.7	5.3	0.094
85.3	32.4	52.9	5.4	0.098
94.3	41.3	53.0	6.9	0.098
105.4	49.2	56.2	8.3	0.104
114.4	57.5	56.9	9.7	0.105
119.2	59.2	60.0	10.0	0.111
131.8	68.4	63.4	11.5	0.118
136.1	73.9	62.2	12.4	0.116
190.7	121.2	69.5	20.4	0.129
262.4	183.3	79.1	30.9	0.148
464.0	280.6	83.4	47.3	0.155

ISOTHERMAL CURVES.

From the experimental data the final or equilibrium concentration of arsenious oxide in the liquid phase was determined in terms of milligram molecules per liter; likewise the number of molecules of arsenious oxide in the solid phase with reference to a single molecule of stannic oxide. Isotherms were then drawn between concentrations as abscissae and molar ratios as ordinates. The data of Tables I and II are represented by the single Curve I-II; the data of Tables III and IV by Curves III and IV respectively. The data of Table VI form a separate graph—Curve VI.

All of the curves appear to be characteristic adsorption isotherms. There are no breaks indicating compounds in the solid phase. On the other hand, at higher concentrations Curve III

runs almost parallel with the axis of concentrations, and the flat portion corresponds closely to the empirical formula $As_2O_3.7SnO_2$ or to Reichard's "compound" $Sn_7As_2O_{17}$. This flat portion alone does not prove anything regarding the real existence of such a compound and the shape of the curve at lower concentrations points apparently to adsorption. The isotherms obtained at low temperatures are roughly similar to the ones Biltz found with hydrousferric oxide; furthermore, an increase of temperature, at least between 21° and 45°, causes a decrease in adsorption, which is normal and is exactly what Biltz observed in his experiments.

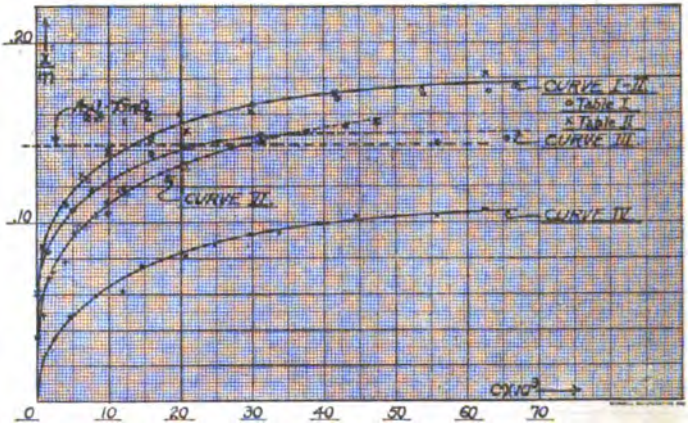

FIG. 1.

Curve VI, representing a temperature of 99° C., also appears to be a typical adsorption isotherm. The arsenious oxide adsorbed from dilute solutions is less than in the previous experiments at lower temperatures, but at higher concentrations of arsenious oxide the reverse appears partly to be true. Some difficulty has been met, however, in getting reliable data for the adsorption at high concentrations, possibly owing to changes in the specific surface of the stannic oxide caused by the peptizing action of adsorbed arsenious oxide. In certain of our experiments, a curious break in the isotherm was noticed and at higher concentrations the curve was apparently flat (parallel to the axis of concentration). It was thought at one time that these observations pointed to adsorption followed by the formation of a definite arsenite, pos-

sibly $As_2O_3.7SnO_2$, but later experiments do not support this view.

In certain of these series it was thought worth while to determine the constants in the simple form of the adsorption isotherm $\left(\frac{x}{m}\right)^n = kC$ and this was done by the usual method of drawing a curve between the logarithms of $\frac{x}{m}$ and C. Values of $\frac{x}{m}$ corresponding to the experimentally determined concentrations were then computed. Inspection of the tables will show that the simple adsorption equation represents the facts well, save at very low and very high concentrations. "Total" adsorption, so-called, as described by Lockemann and Paucke[10] was never observed.

REVERSIBILITY.

Adsorption is a reversible process, provided no secondary irreversible changes interfere. To test the reversibility in the present instance, three mixtures were prepared as follows:

Mixture	1	2	3
As_2O_3 solution (263 mg As_2O_3)	25 cc.	25 cc.	25 cc.
SnO_2 suspension (395 mg SnO_2)	5 cc.	5 cc.	5 cc.
Water	30 cc.	none	none

The mixtures in bottles were set aside for 24 hours and allowed to reach equilibrium. Then 30 cc. of water were added to No. 2 and all three were shaken in the machine for one-half hour. The results were as follows:

Mixture	As_2O_3 Adsorbed
1	83.5 mg
2	82.8 mg
3	89.4 mg

Since 1 and 2 are very nearly identical so far as adsorbed arsenic is concerned, the process is a reversible one. From other experiments, not given here in detail, it appears that adsorbed arsenious oxide is returned to the diluted solution rather less

[10] Zeit. Kolloidchemie (1911), 8, 273.

rapidly than it is adsorbed originally, and the longer the time allowed for equilibrium to be reached before diluting, the slower is the return of adsorbed arsenic into solution.

PEPTIZATION BY ADSORBED ARSENIOUS OXIDE.

Bancroft[11] has pointed out that strong adsorption of salt from solution should tend to peptize the adsorbing substance. Adsorbed arsenious oxide should therefore peptize stannic oxide. To test this point 25 cc. of distilled water were mixed with 5 cc. of the stannic oxide suspension. After two hours the oxide had settled completely, leaving the supernatant liquid perfectly clear. When 25 cc. of a fairly strong solution of arsenious oxide were mixed with 5 cc. of the suspension, several days were required for the stannic oxide to settle. Throughout this work there was noted a strong tendency for the finely divided oxide to remain persistently suspended in the more concentrated solutions of arsenious acid.

SUMMARY.

The results of this paper may be summarized as follows:

1. At ordinary temperatures metastannic acid adsorbs arsenious oxide from solution. As the temperature rises adsorption decreases. There is no trustworthy evidence at present that definite arsenites are formed and it is probable that Reichard's "basic arsenite" is an adsorption compound.

2. At ordinary temperatures metastannic acid adsorbs arsenious oxide from solutions containing sulphuric acid or sulphuric acid and copper sulphate. The presence of sulphuric acid tends to cut down the adsorption.

3. The old Gruessner and Badt method of removing arsenic from spent electrolyte appears to be an adsorption process. The presence of other impurities more strongly adsorbed than arsenious oxide should decrease the adsorption of the latter and may account for the lack of reliability of the process, a deficiency which was long ago pointed out by Addicks. In such a process of adsorption, also, the physical condition of the metastannic acid would be a factor of prime importance.

[11] Journ. Phys. Chem. (1916), 20, 85.

4. The adsorption equilibrium is reached relatively rapidly even at ordinary temperatures and it is reversible.

5. Adsorbed arsenious oxide has a decided peptizing action on metastannic acid.

Further experiments are in progress.

Cornell University,
March, 1920.

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